Pulsed EPR Study of Porphyrin-Functionalized Graphene Nanoribbons

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Department of Materials, Trinity College
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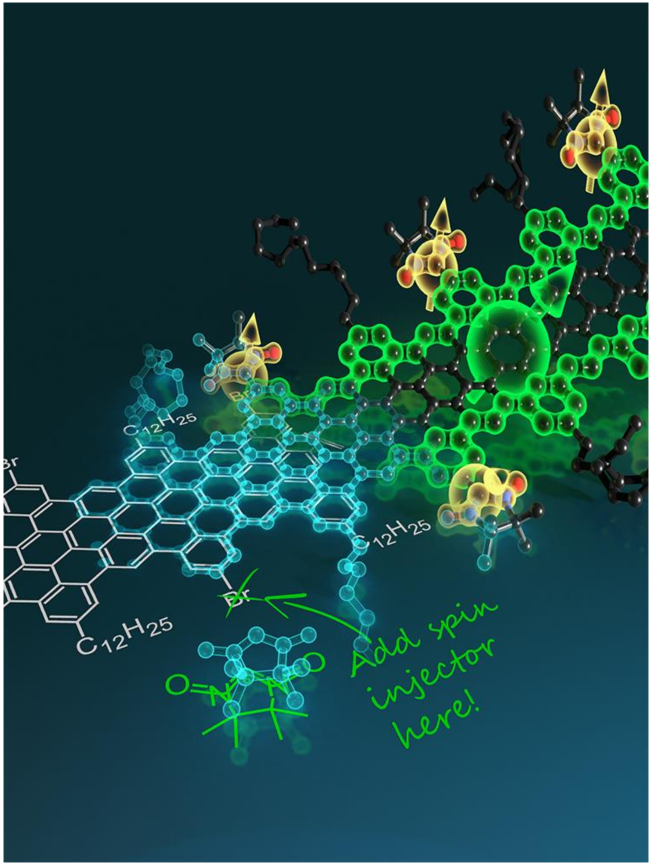
27/07/2022

Graphene Nanoribbons (GNRs)



- Fascinating electronic properties
  - Tunable band gap
  - Spin-filtering zigzag edge states
  - Topological phase
- Long spin coherence time
- Bottom-up synthesis approach

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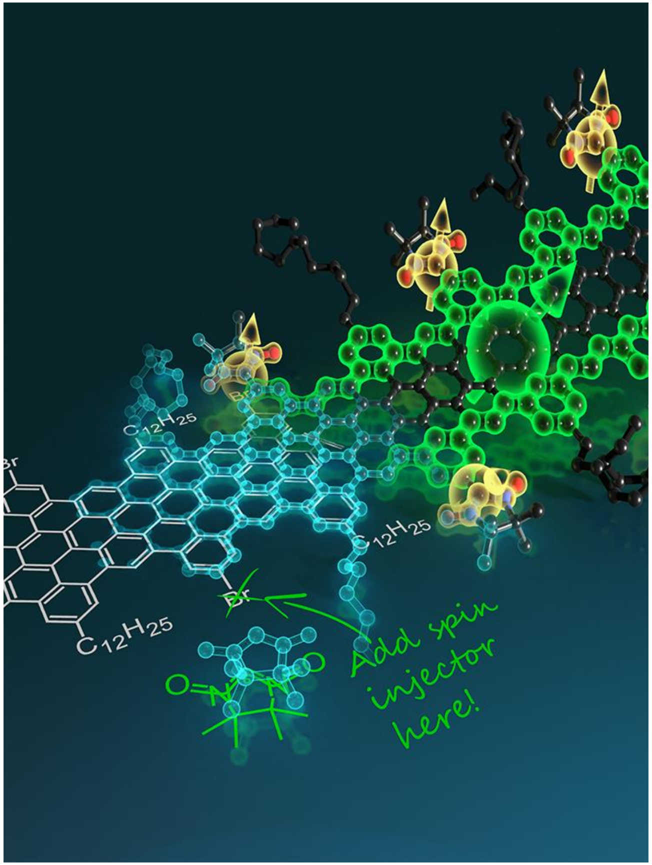

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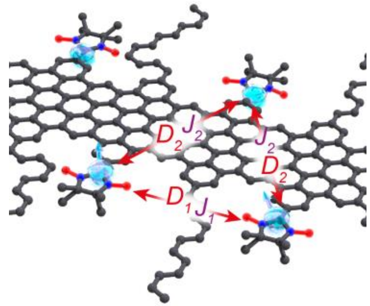

Nitronyl nitroxide-functionalized graphene nanoribbon (NIT-GNR)

LETTER

https://doi.org/10.1038/s41586-018-0154-7

Magnetic edge states and coherent manipulation of graphene nanoribbons

Michael Slota[1,2], Ashok Keerthi[3], William K. Myers[2], Evgeny Tretyakov[4], Martin Baumgarten[3], Arzhang Ardavan[2,5], Hatef Sadeghi[6], Colin J. Lambert[6], Akimitsu Narita[3], Klaus Müllen[3] & Lapo Bogani[1,2]*

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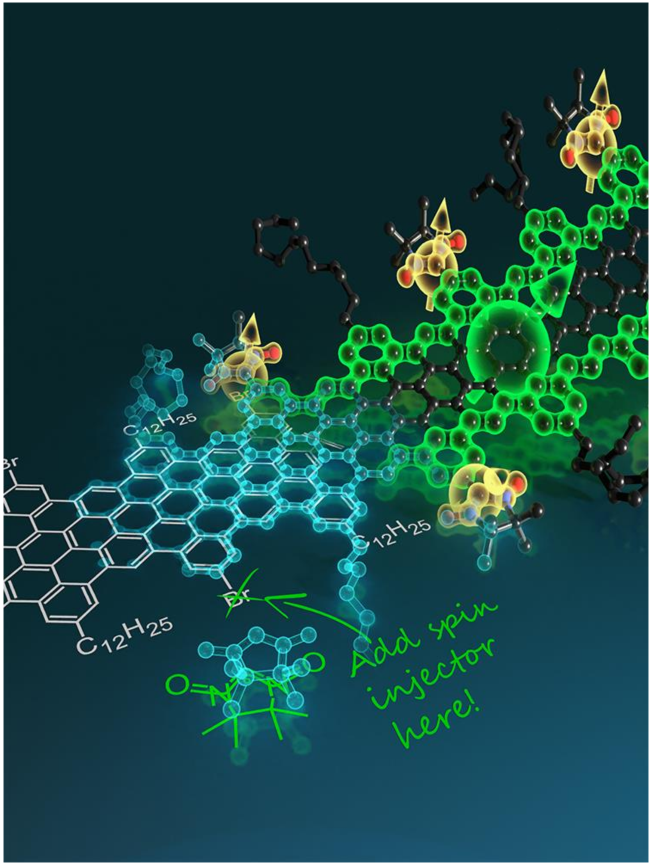

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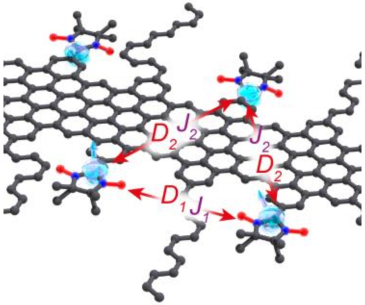
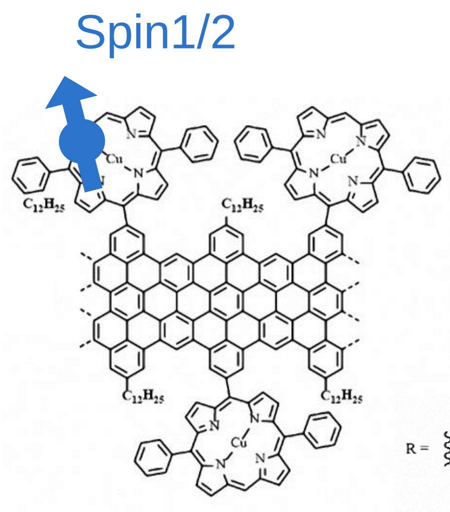


Nitronyl nitroxide-functionalized graphene nanoribbon (NIT-GNR)

- Introduce spin states using other functionalized groups?
- Can we improve Tm?

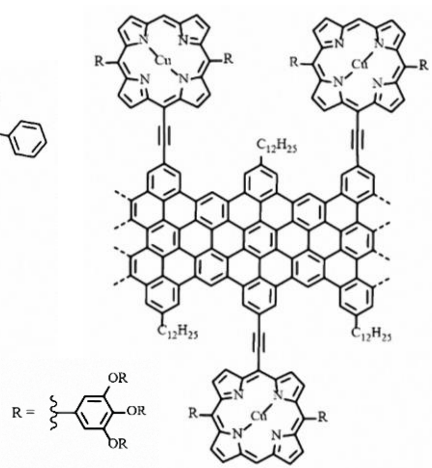
Porphyrin-Functionalized GNRs

- Adjustable metal centers



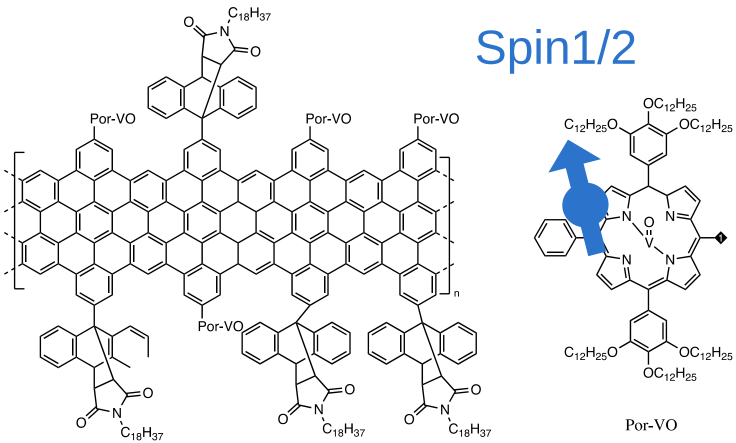
Suz-Cu-GNR, 1

Single bonds
(Suzuki coupling)



SG-Cu-GNR, 2

Triple bonds
(Sonogashira coupling)

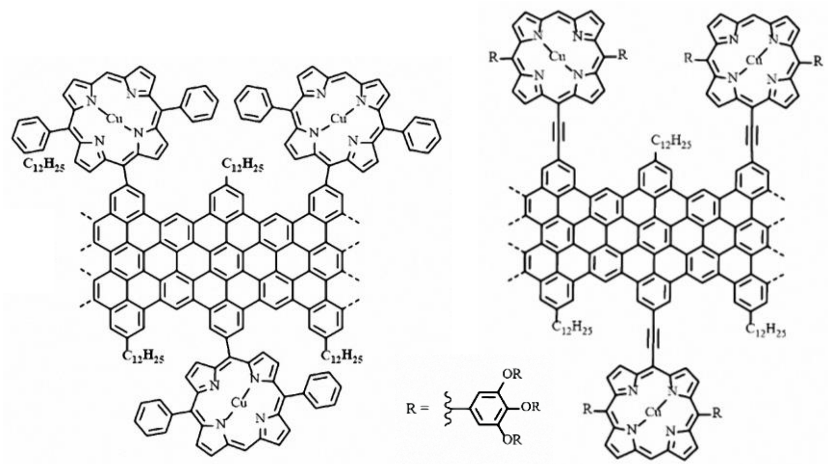


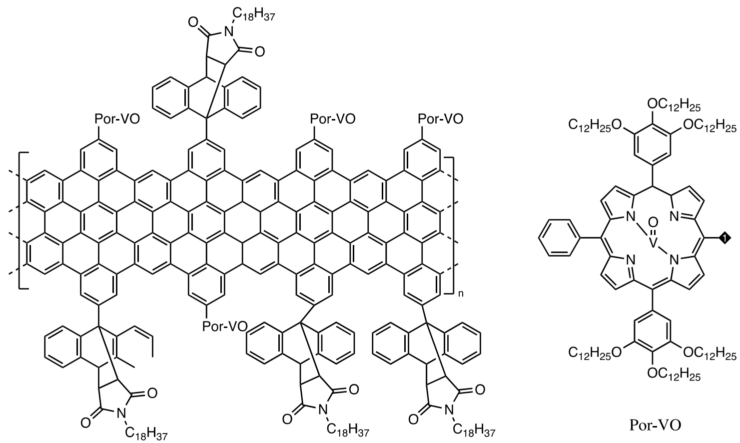
VO-GNR

Synthesized by Alicia Götz, Xuelin Yao, Dimitris Alexandropoulos

Porphyrin-Functionalized GNRs

- Adjustable metal centers





Suz-Cu-GNR, 1	**SG-Cu-GNR, 2**
Single bonds (Suzuki coupling)	Triple bonds (Sonogashira coupling)

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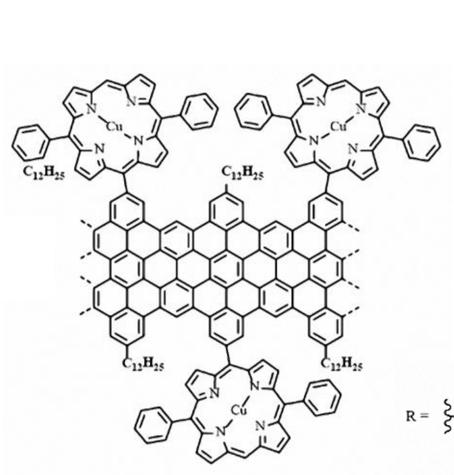
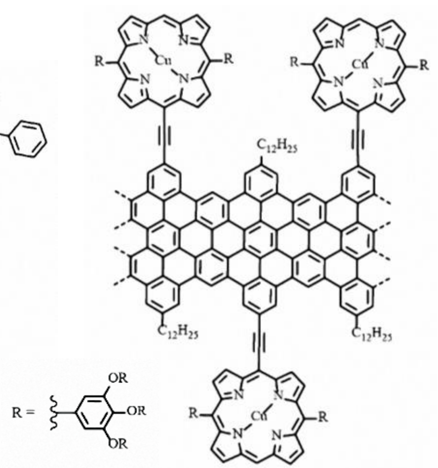
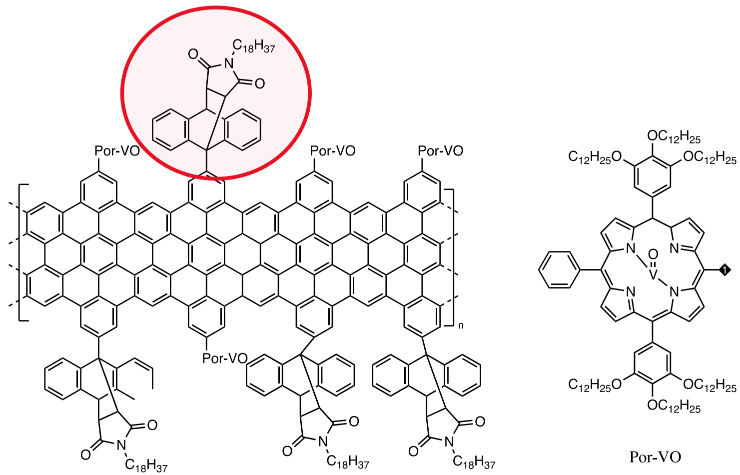
Porphyrin-Functionalized GNRs

- Adjustable metal centers

Bulky group to enhance solubility







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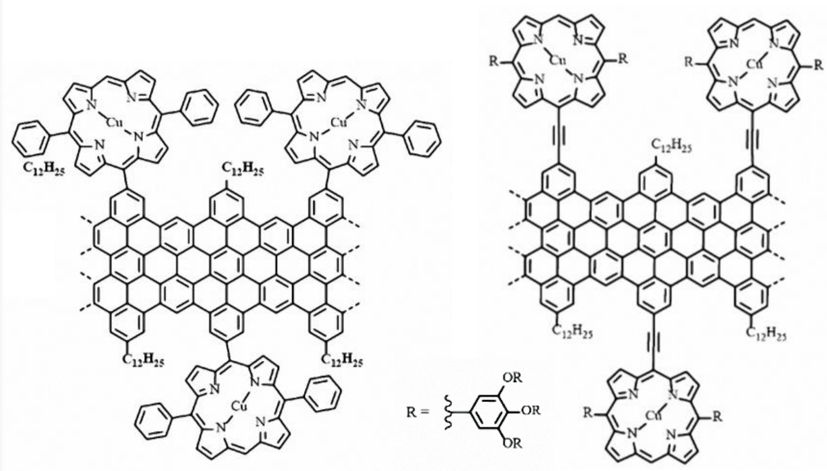

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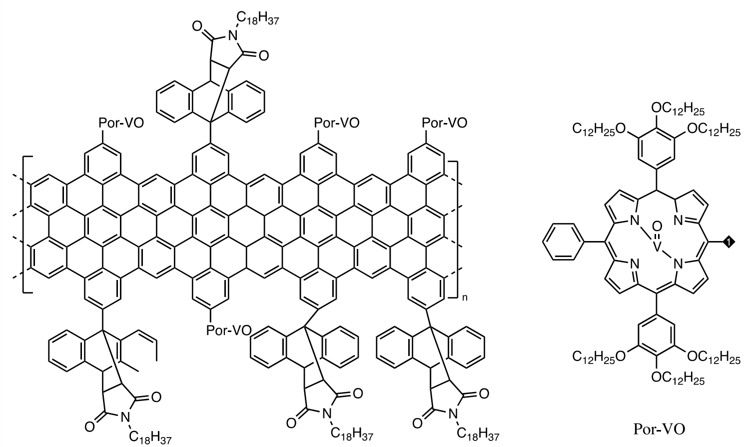
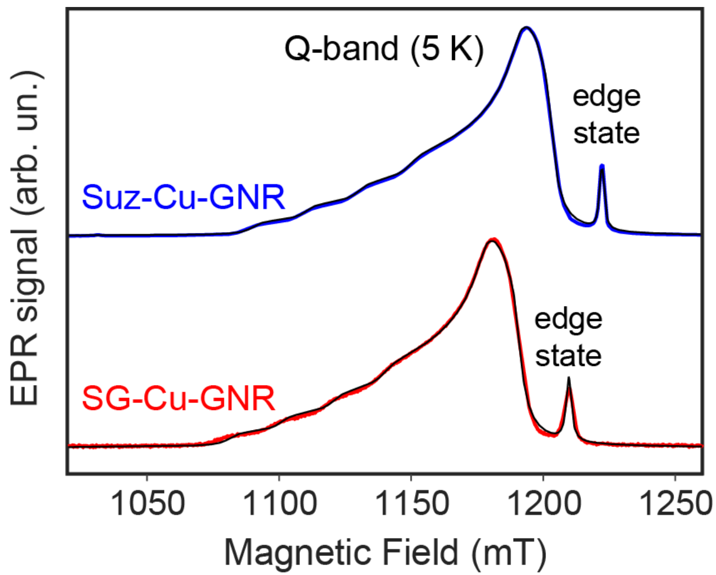


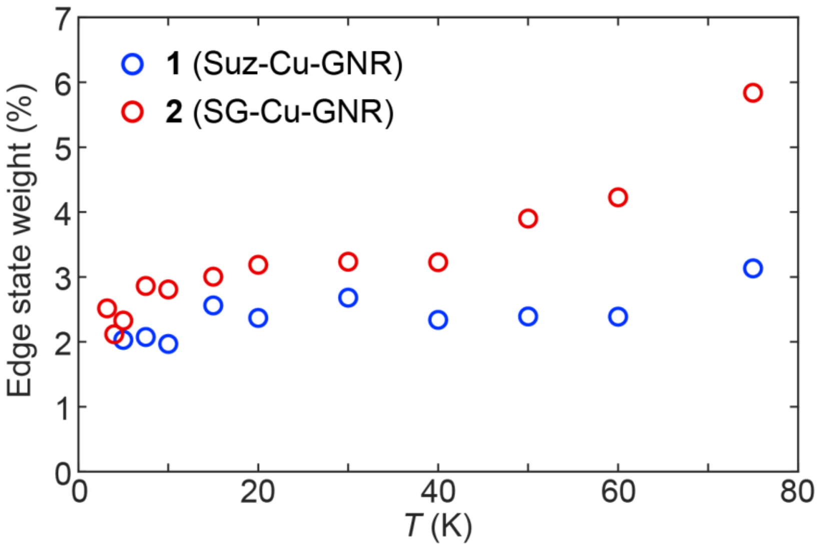
VO-GNR

Powders

Powders and solutions (tetralin)

EPR Spectra of Cu-GNRs





- Perfect fit using EASYSPIN
- Additional sharp peak attributed to spin states in GNRs
- Triple-bonds seem to provide a larger spin-injection efficiency

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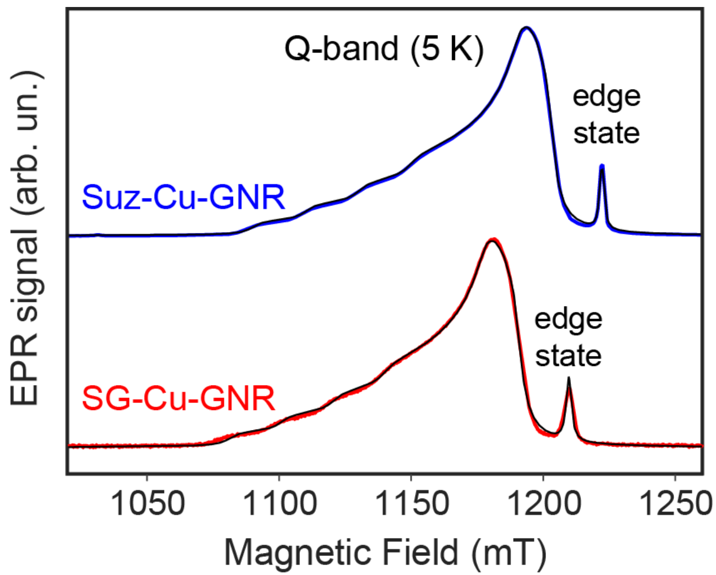

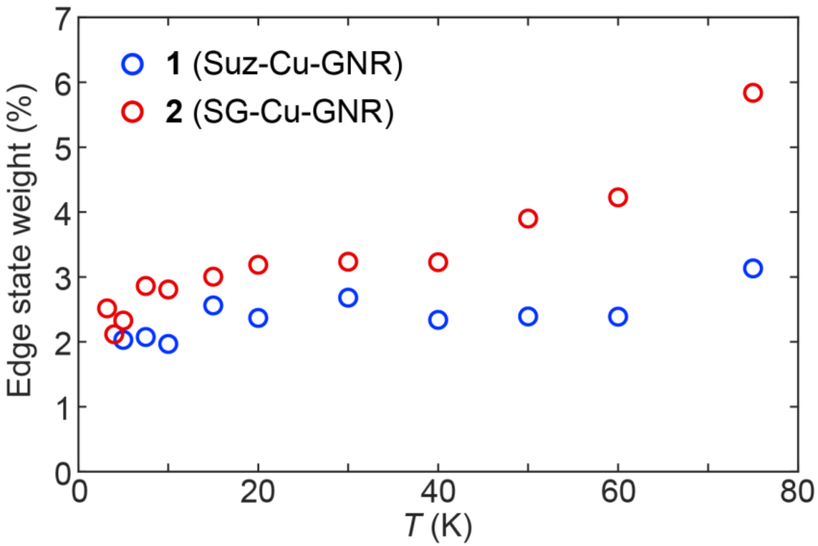

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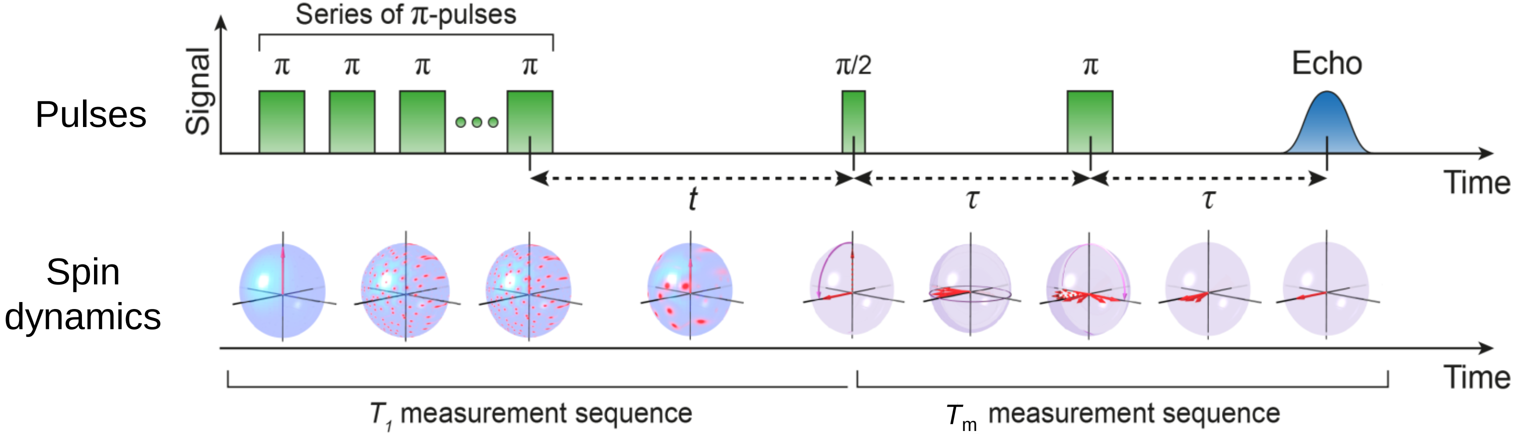
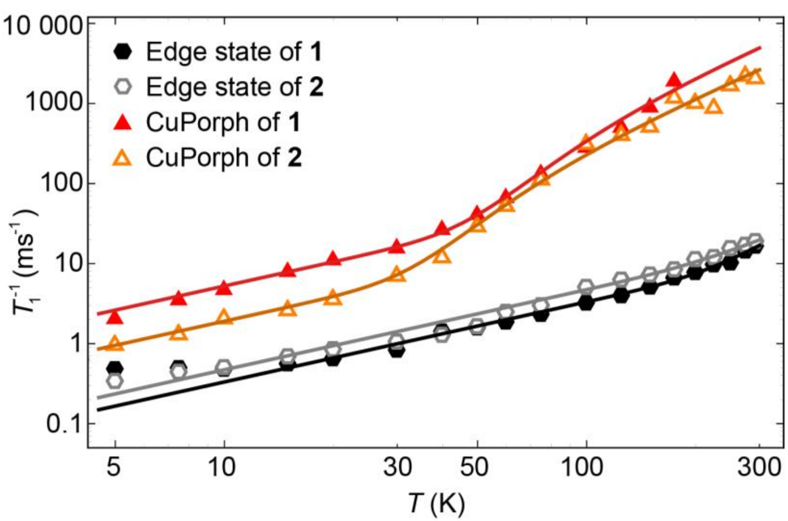
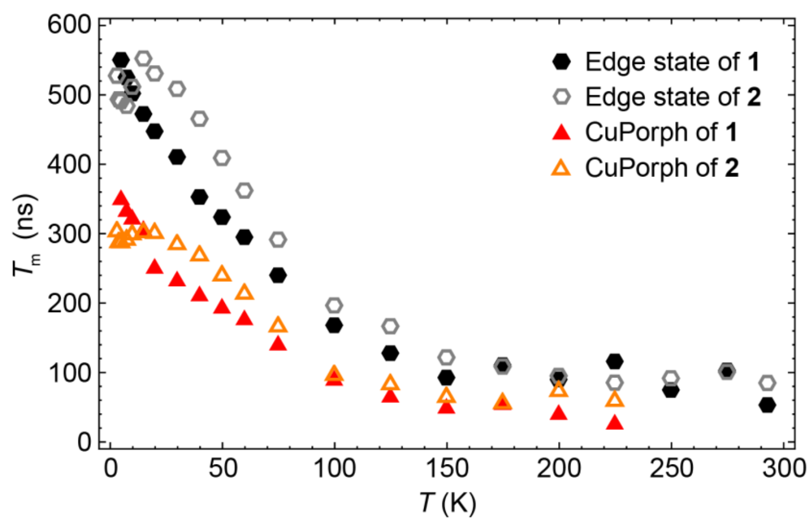
Parameter	Suz-Cu-GNR	SG-Cu-GNR
$g_{\parallel,Cu}$ $g_{\perp,Cu}$	2.045(1) 2.186(1)	2.044(1) 2.182(1)
$A_{\parallel,Cu}$ $A_{\perp,Cu}$	86 $\pm$ 10 MHz 600 $\pm$ 10 MHz	89 $\pm$ 10 MHz 595 $\pm$ 10 MHz
$g_{iso,edge}$	2.0033(3)	2.0016(3)

Spin Dynamics of Cu-GNRs







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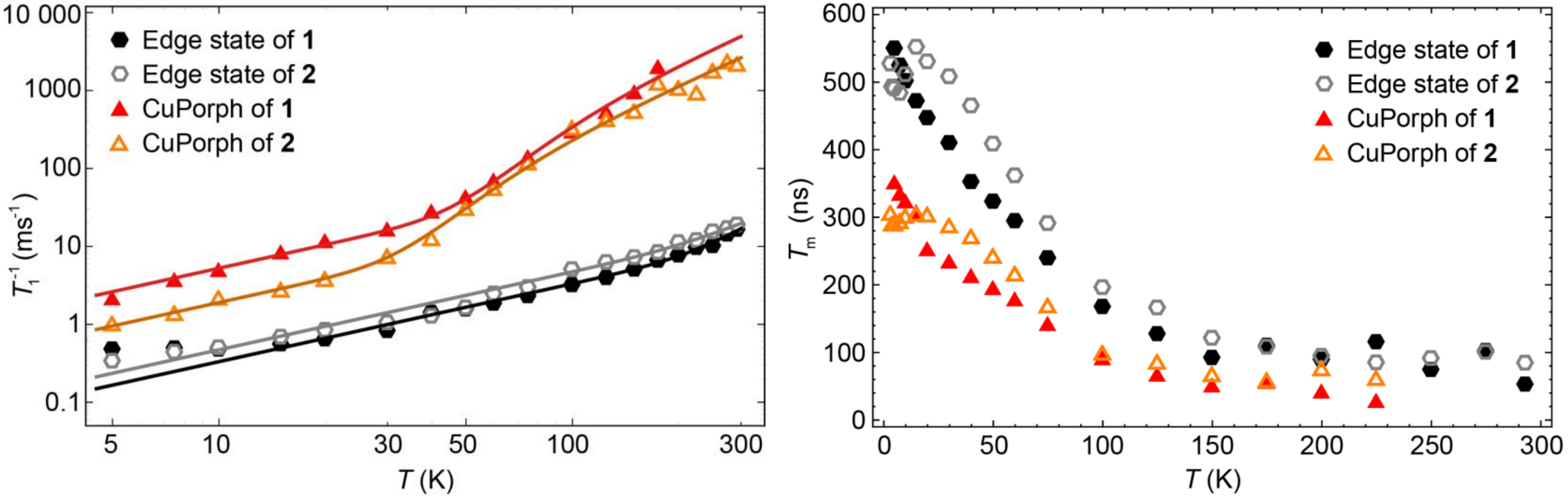

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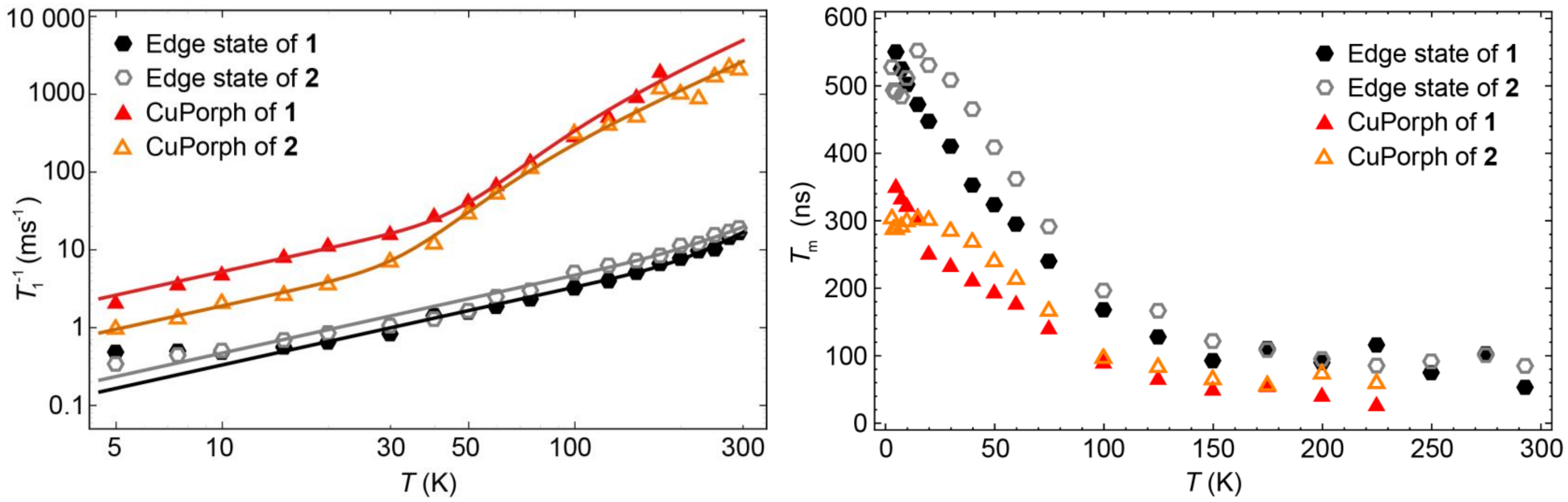
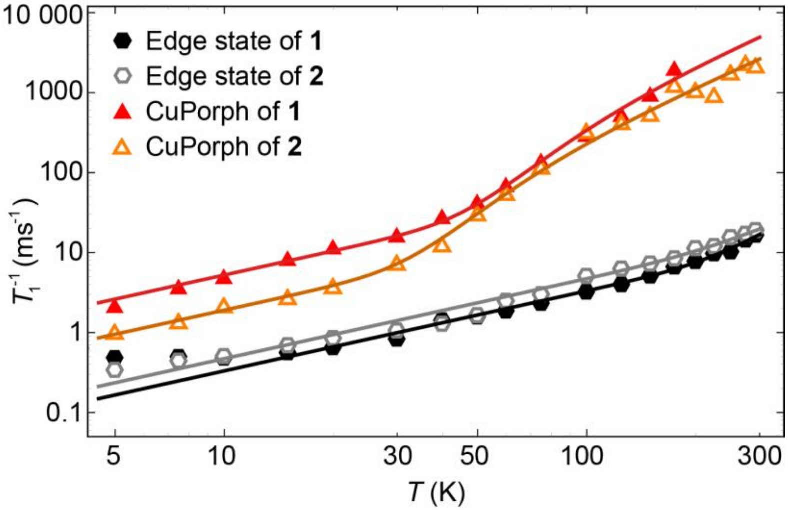
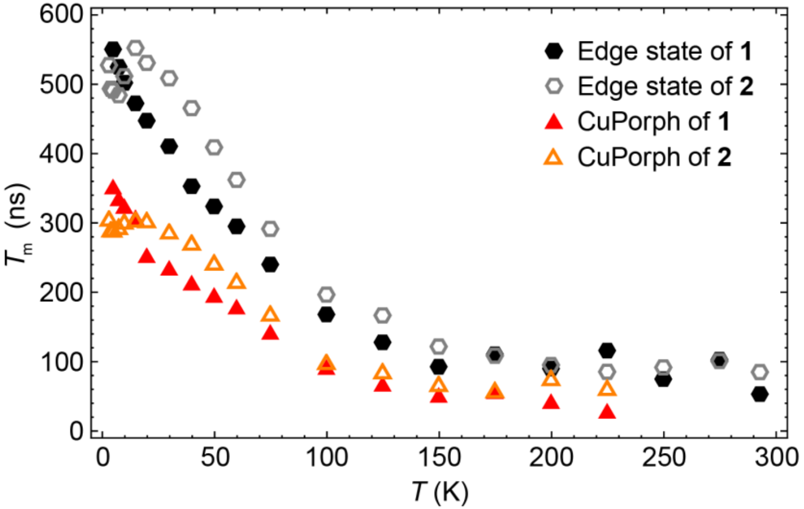


- Edge state shows larger spin–lattice relaxation times than the Cu spins
- These spins show both direct and Raman relaxation
- The relaxation of the edge state is significantly different, likely a direct result of the coupling to the carbon lattice

Spin Dynamics of Cu-GNRs





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- Edge state shows larger Tm than Cu spins
- No effects of spin injection on the spin dynamics

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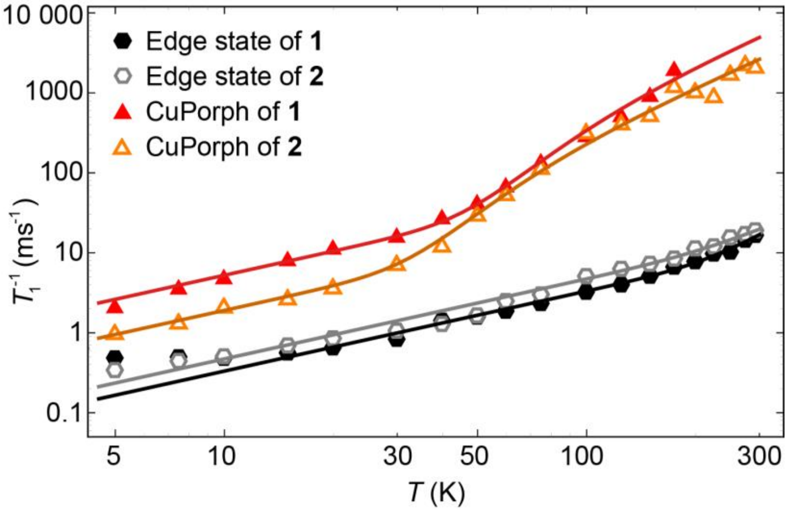

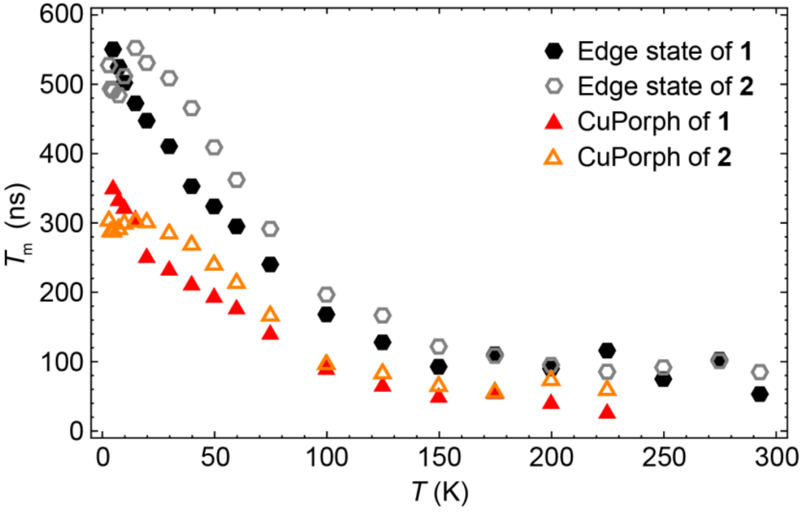

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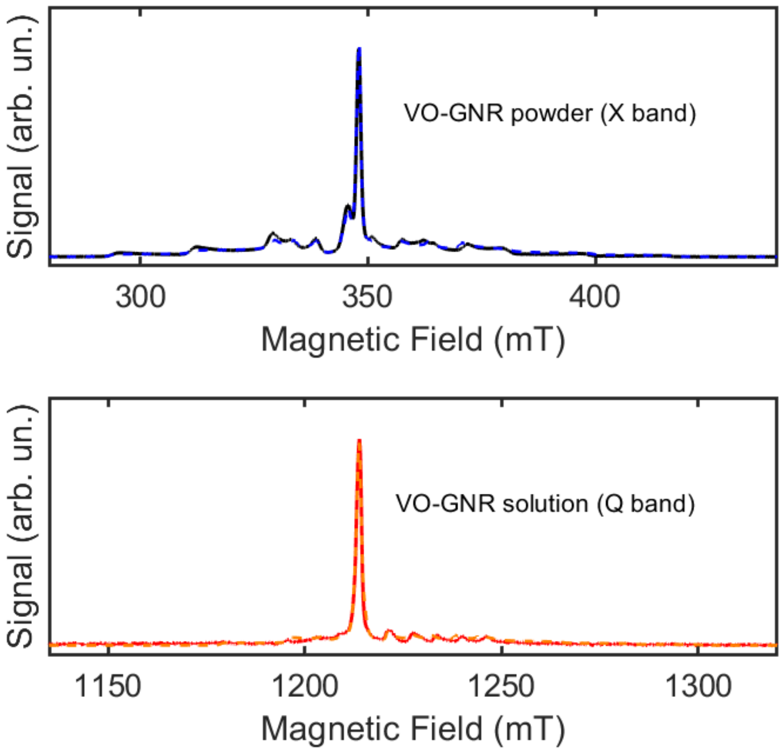
- Edge state shows larger Tm than Cu spins
- No effects of spin injection on the spin dynamics were observed

However, the Cu-GNRs are not soluble…

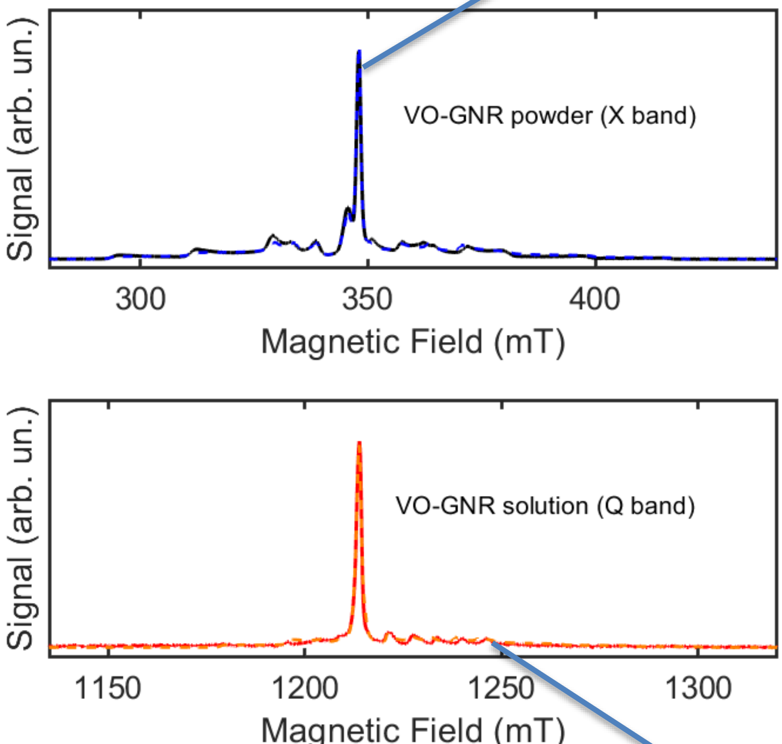
EPR Spectra of VO-GNR



Parameter	VO-GNR powder	VO-GNR solution
$g_{\parallel,V}$ $g_{\perp,V}$	1.981(1) 1.958(2)	1.983(2) 1.961(2)
$A_{\parallel,V}$ $A_{\perp,V}$	166 $\pm$ 1 MHz 476 $\pm$ 1 MHz	155 $\pm$ 2 MHz 477 $\pm$ 7 MHz
$g_{iso,edge}$	1.9991(1)	2.001(1)

EPR Spectra of VO-GNR

Peak from **edge states** in GNR



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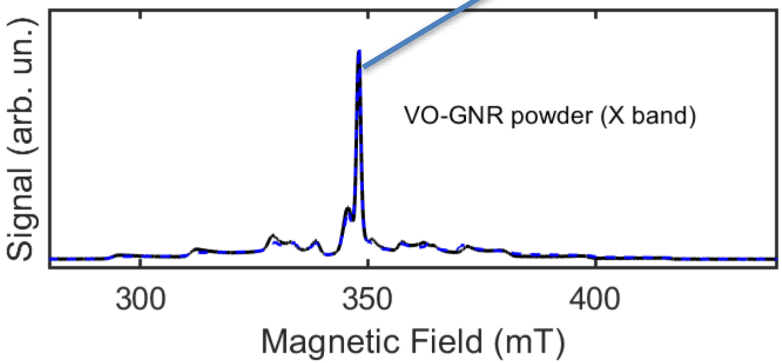
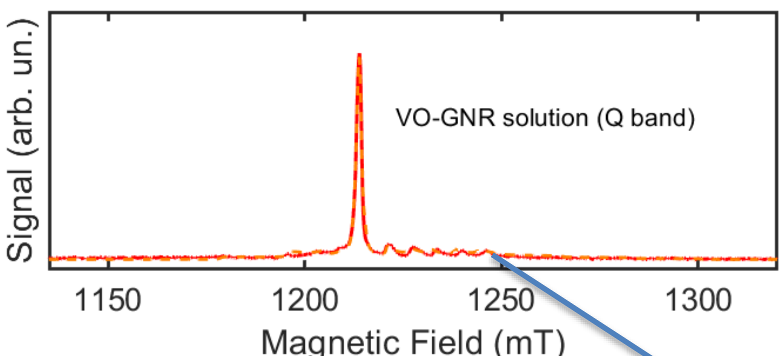
8 peaks from hyperfine coupling
(Vanadyl nuclear spin I = 7/2)

EPR Spectra of VO-GNR

Peak from **edge states** in GNR, what if they are defects?





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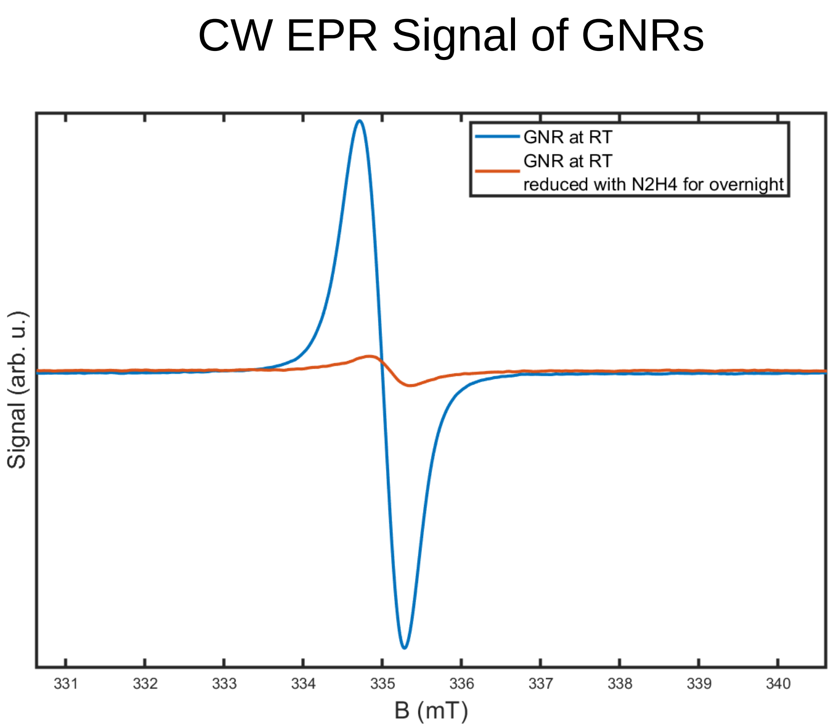
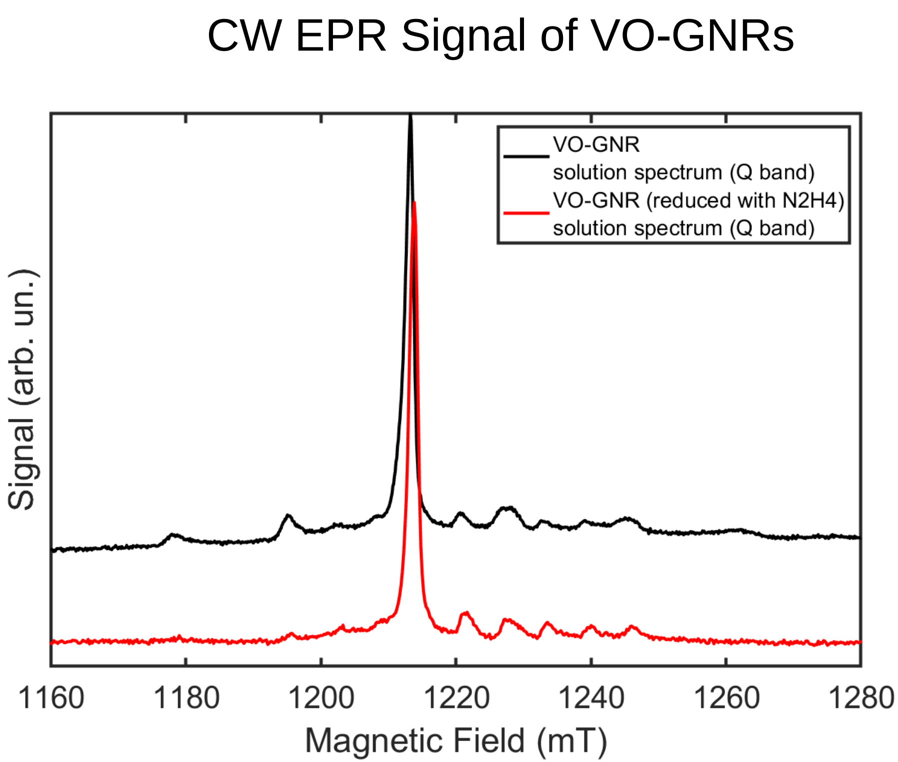
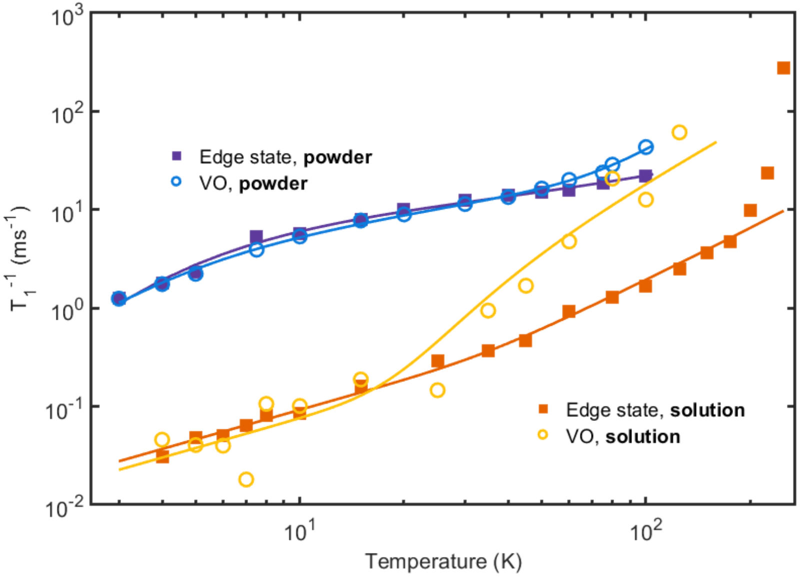


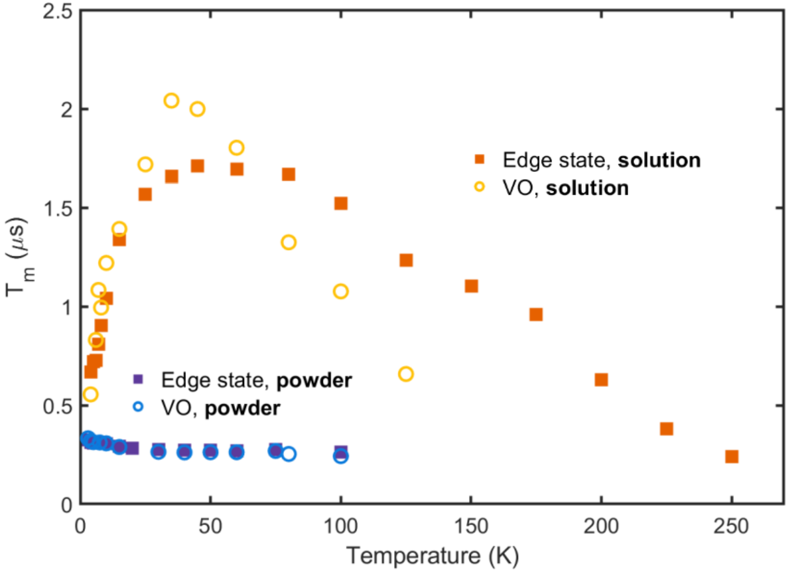


- Residue defects in GNRs are greatly reduced by hydrazine.
- Edge state peak of VO-GNRs persists after being reducing.

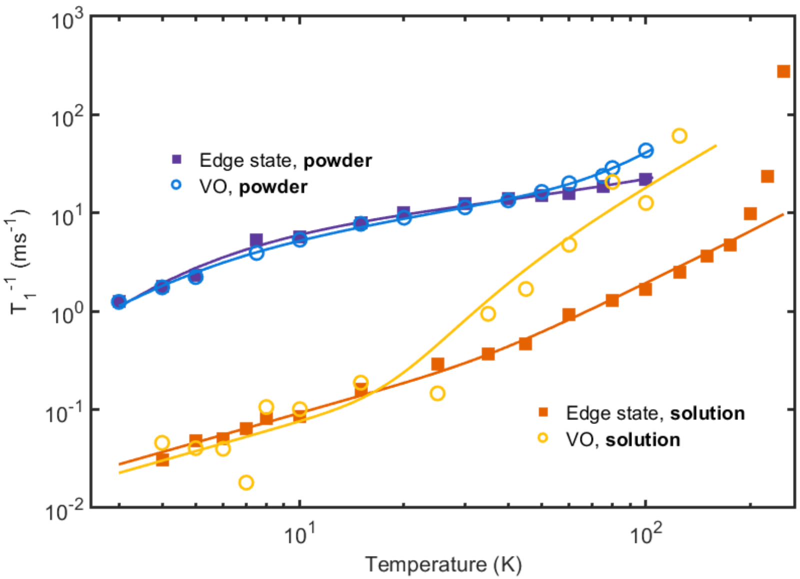
→ Rules out the influence of defects in GNR backbone.

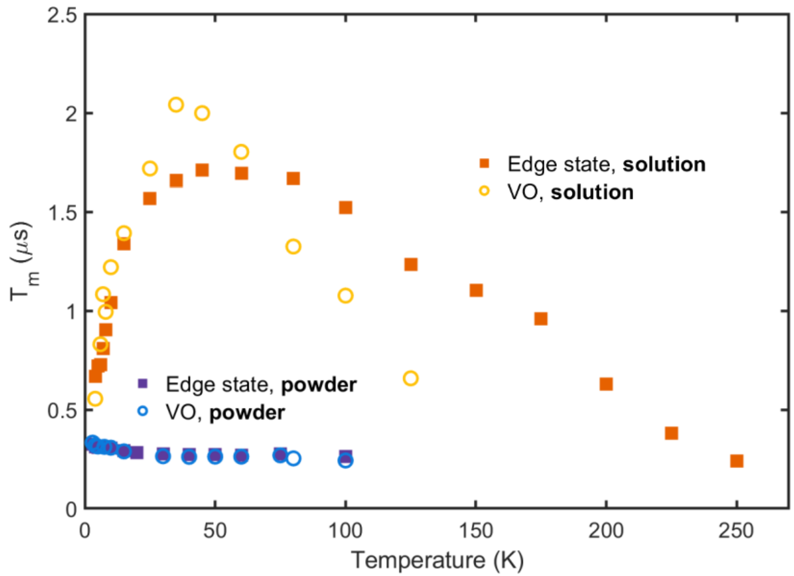
Spin Dynamics of VO-GNR





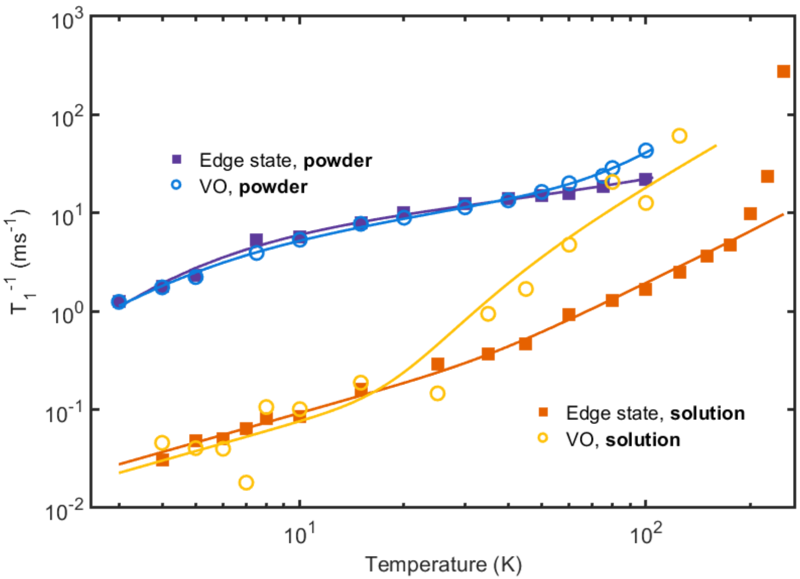
Spin Dynamics of VO-GNR

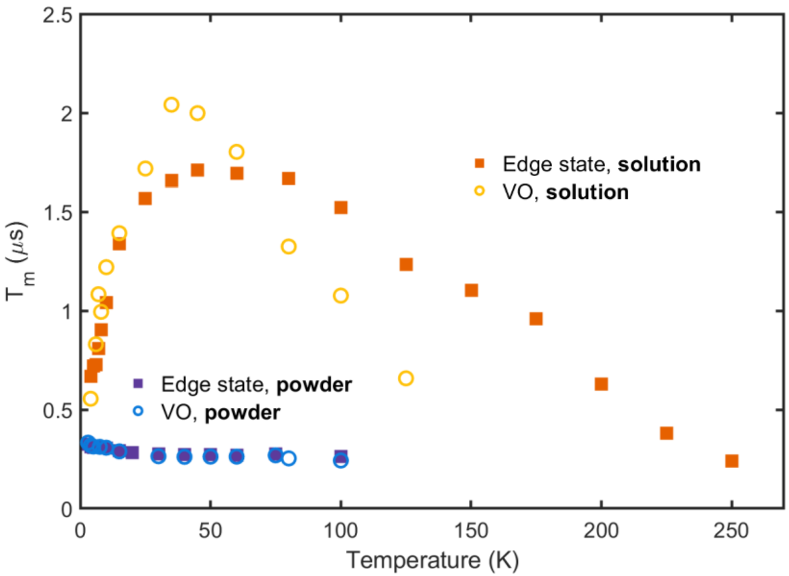




- T_1 of solution sample is **two orders** higher than powder sample
- Edge state and VO spins show different relaxation behaviours.
- The T_1 of VO spin decreases faster with temperature.

Spin Dynamics of VO-GNR





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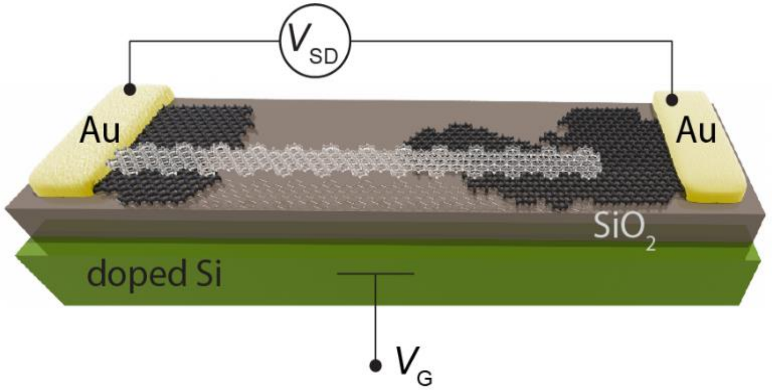
- Edge state and VO spins show different relaxation behaviours.
- The T_1 of VO spin decreases faster with temperature.

- Tm of powder samples are similar as Cu-GNRs
- Tm of solution sample is **one order** higher than powder sample
- The maximum Tm reaches 2 μs at around 35 K

Conclusion

- Porphyrins work as efficient spin injectors when grafted to graphene nanoribbons. Both single and triplet bond connections lead to spin states in GNRs.
- Bulky groups can significantly improve the solubility and thus enhance the spin coherence time by one order of magnitude.
- Graphene nanoribbons can be the testbed for creating more functional molecules by rational design of the structure.
- Integrating functionalized GNRs into single molecule devices.



Acknowledgements

University of Oxford

Lapo Bogani
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Dimitris Alexandropoulos
Michael Slota
Karen Yan
William Myers

Max Planck Institute for Polymer Research, Mainz

Ashok Keerthi
Martin Baumgarten
Klaus Müllen

Novosibirsk Institute of Organic Chemistry

Evgeny Tretyakov

OIST

Akimitsu Narita
Alicia Götz

THE ROYAL SOCIETY

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Centre for Advanced Electron Spin Resonance

Max-Planck-Institut für Polymerforschung
Max Planck Institute for Polymer Research

EPSRC
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