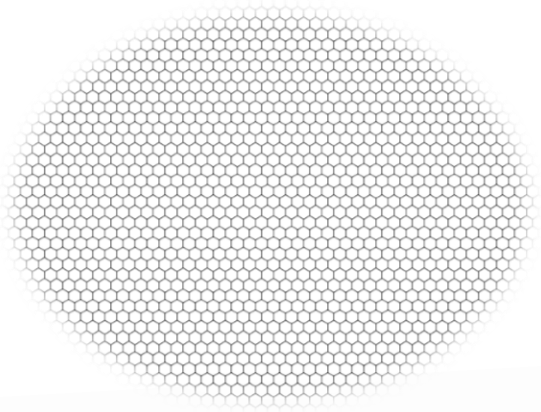
Molecular Nanographene as Quantum Units

Fanmiao Kong

21/06/2022

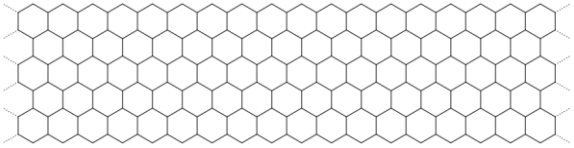
Magnetic Zigzag Edge States in Graphene Nanoribbon

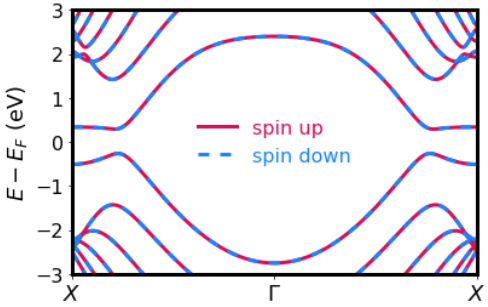
2D graphene



“Cutting”

1D zigzag graphene nanoribbon





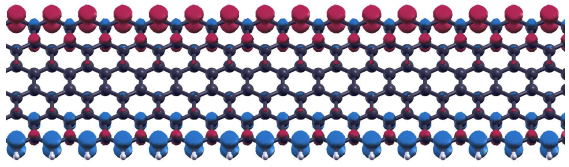
Band structure

Gapless

Band structure

Spin up

Spin down



- Band gap
- Spin-polarized zigzag edge states

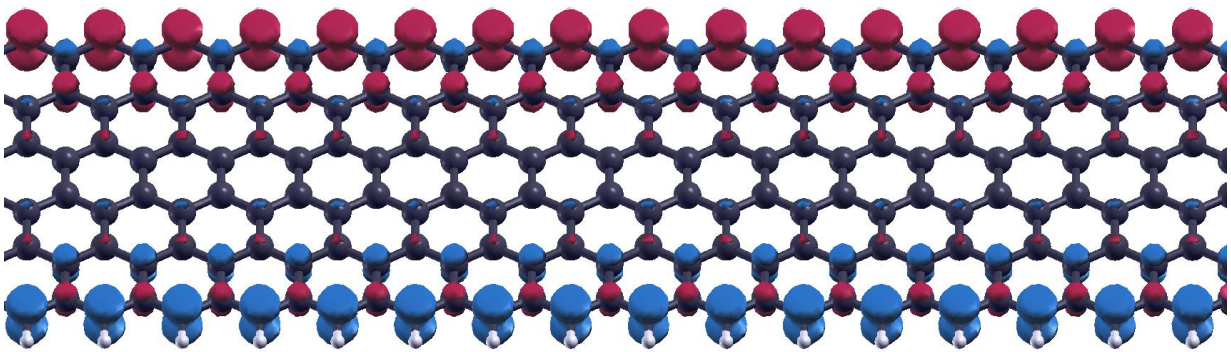
Magnetic Zigzag Edge States in Graphene Nanoribbon

- ✓ Useful for spintronic devices
- ✓ Predicted to have **long spin coherence time**

J. Fischer, B. Trauzettel, D. Loss, *Physical Review B 80, 155401 (2009).*

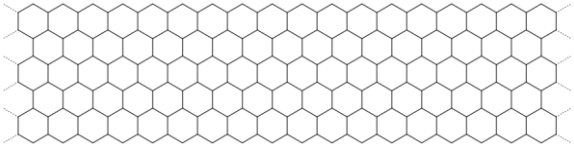
- ✗ Synthesized in high vacuum. Chemically unstable
- ✗ Difficult to study the spin states

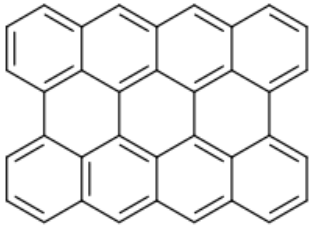
P. Ruffieux *et al., Nature 531, 489 (2016)*



Zigzag Edge in Nanographene Molecule

1D zigzag graphene nanoribbon

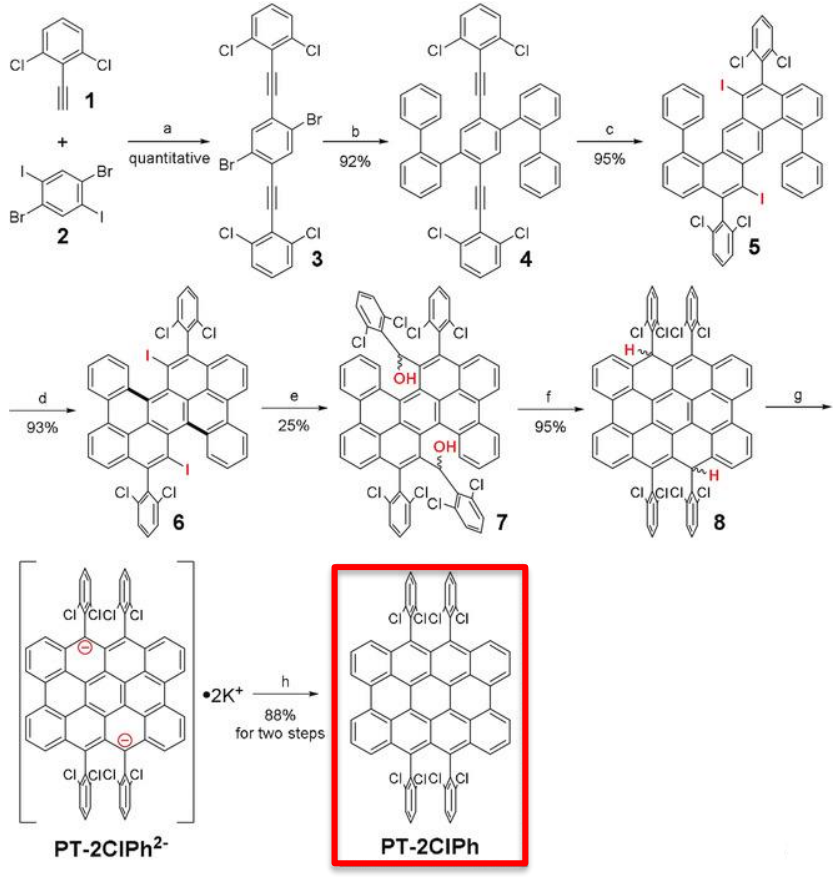




0D nanographene molecule

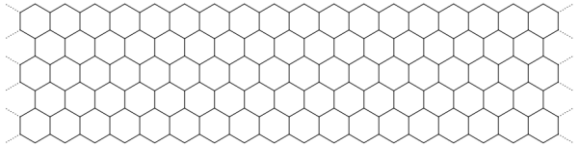
Zigzag Edge in Nanographene Molecule

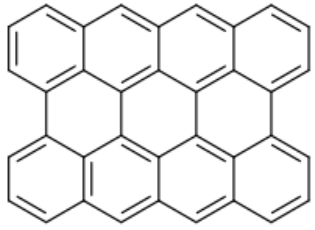
Synthesized by Jishan Wu's group at NUS



Y. Ni *et al., Angewandte Chemie 130, 9845-9849 (2018)*

1D zigzag graphene nanoribbon

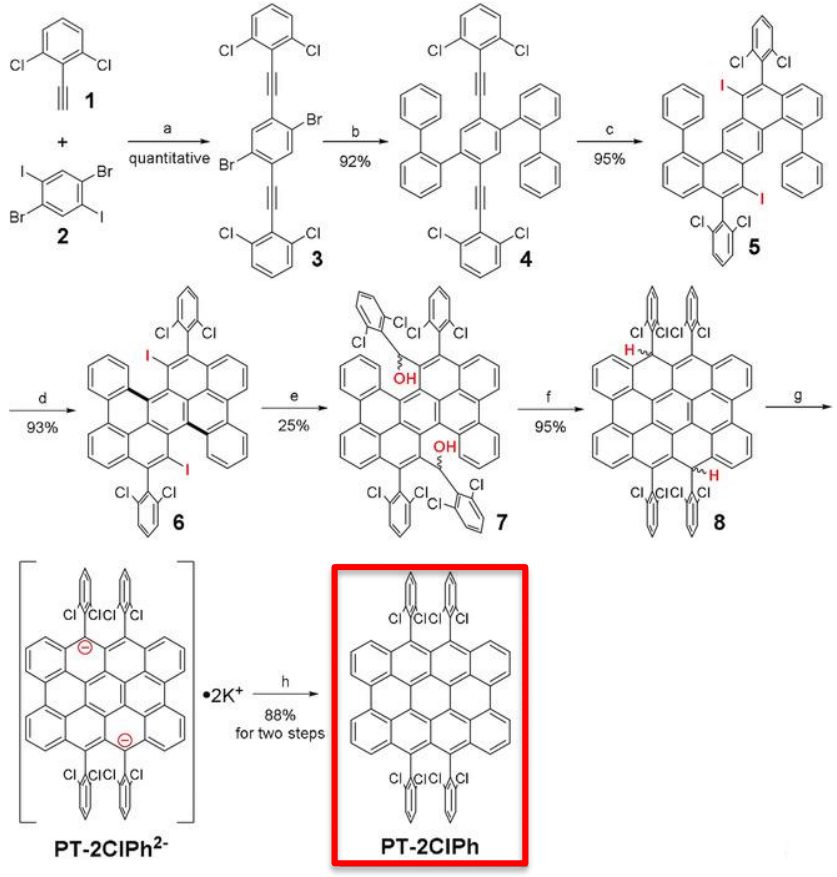




0D nanographene molecule

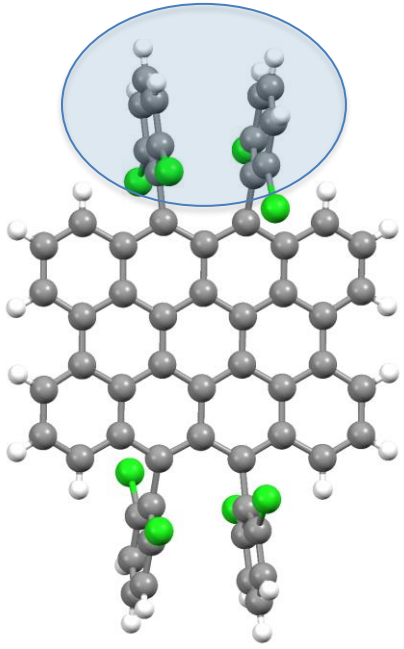
Zigzag Edge in Nanographene Molecule

Synthesized by Jishan Wu's group at NUS



Y. Ni *et al., Angewandte Chemie 130, 9845-9849 (2018)*

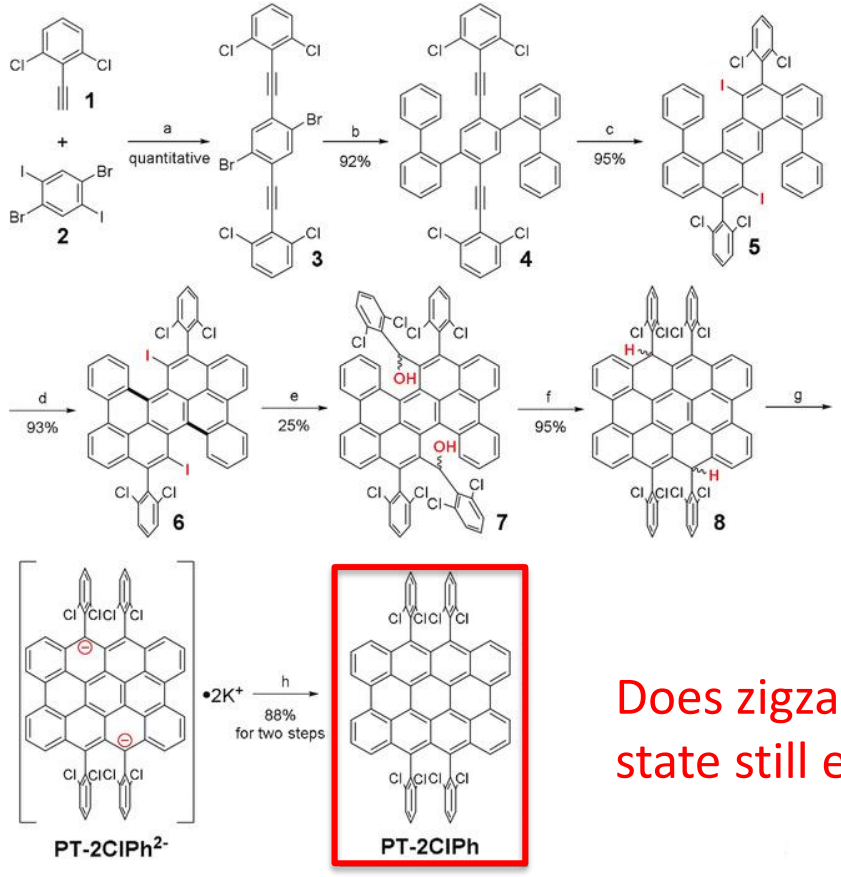
Bulky group to enhance stability and solubility



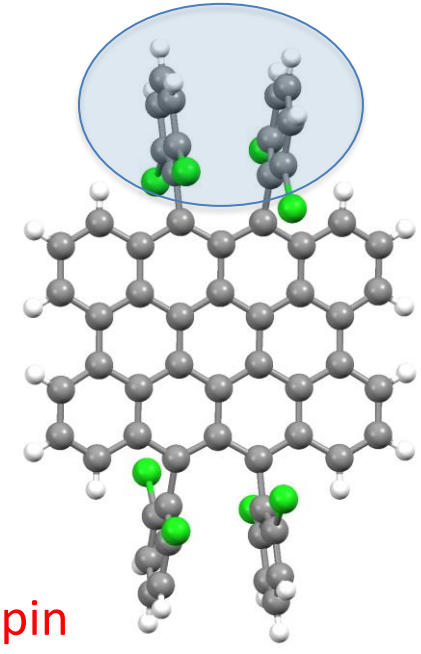
Peri-tetracene

Zigzag Edge in Nanographene Molecule

Synthesized by Jishan Wu's group at NUS



Bulky group to enhance stability and solubility



Peri-tetracene

Does zigzag edge spin state still exist?

Y. Ni *et al., Angewandte Chemie 130, 9845-9849 (2018)*

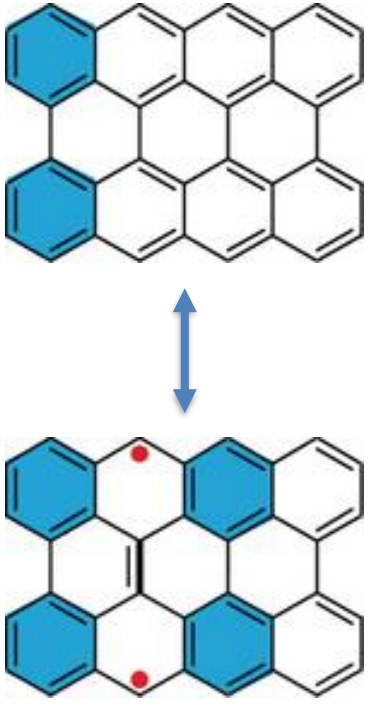
Peri-tetracene

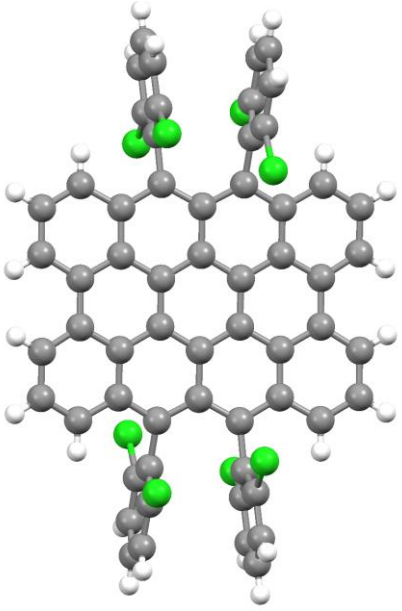
Clar's sextet rule:

More aromatic rings

→ More stable

52.5% diradical character





Peri-tetracene

Y. Ni *et al., Angewandte Chemie 130, 9845-9849 (2018)*

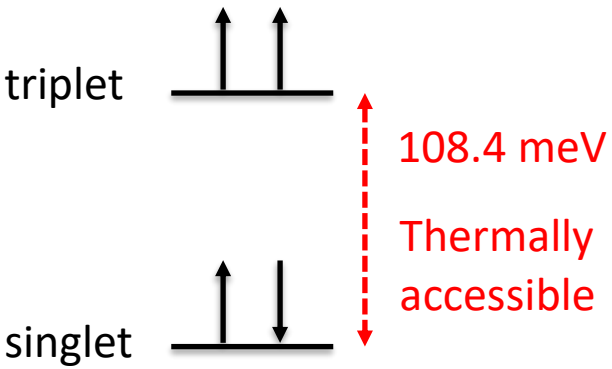
Peri-tetracene

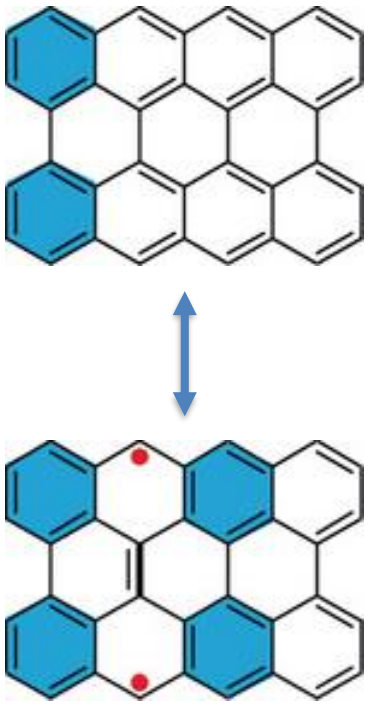
Clar's sextet rule:

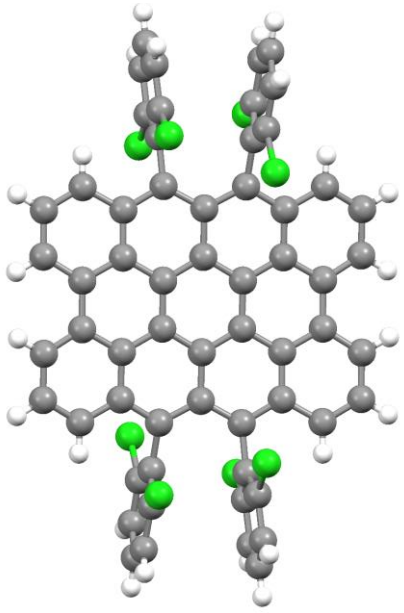
More aromatic rings

→ More stable

52.5% diradical character



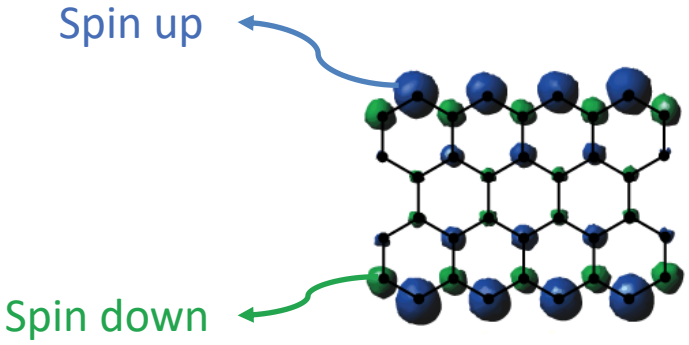




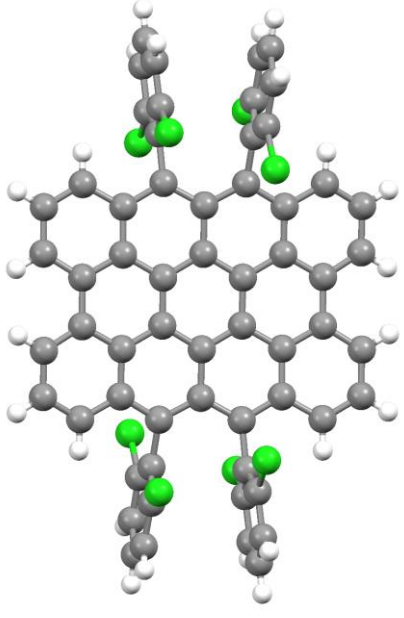
Peri-tetracene

Y. Ni *et al., Angewandte Chemie 130, 9845-9849 (2018)*

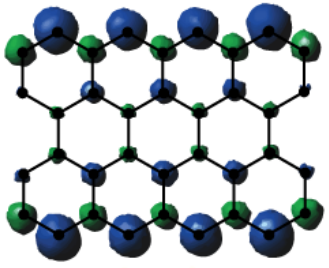
Peri-tetracene



Spin density of triplet state

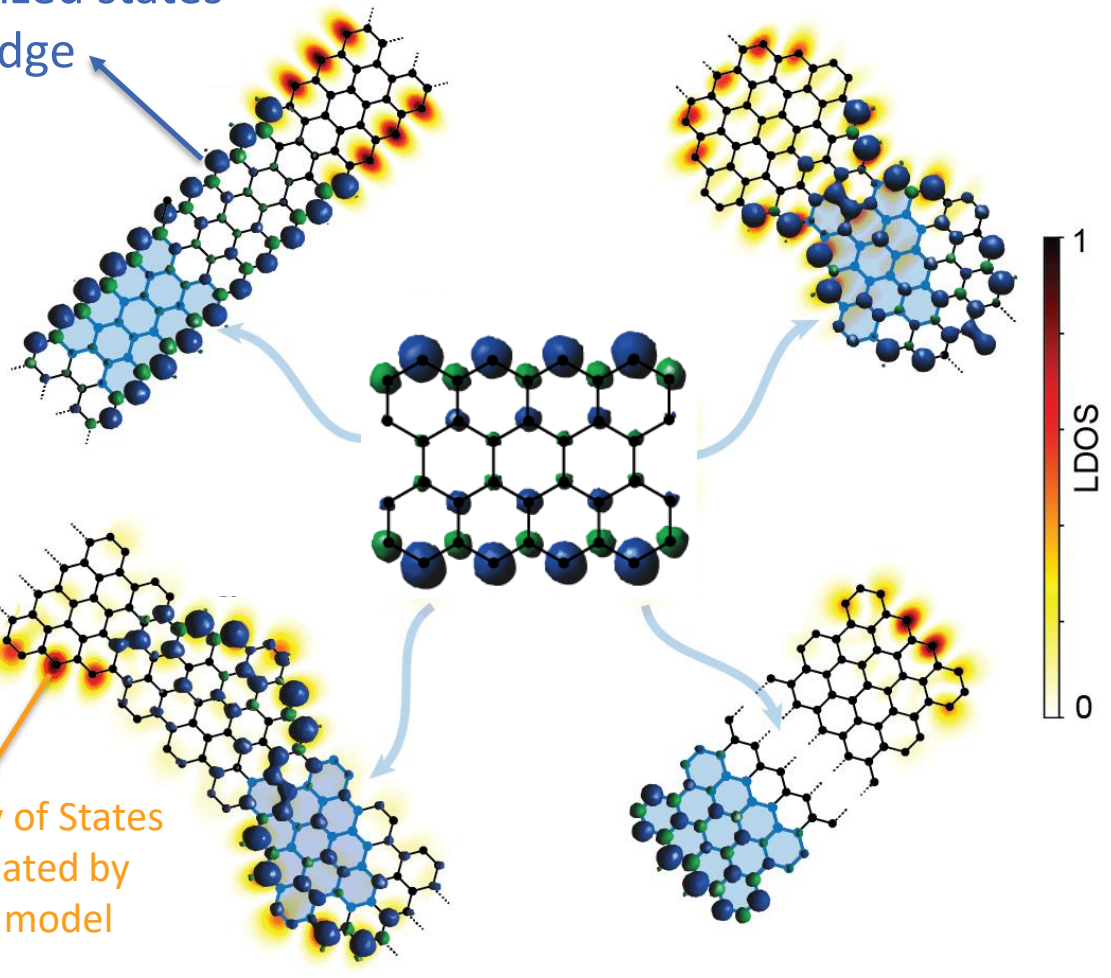


Zigzag Edge in Extended Structures



Zigzag Edge in Extended Structures

Spin-polarized states
in zigzag edge

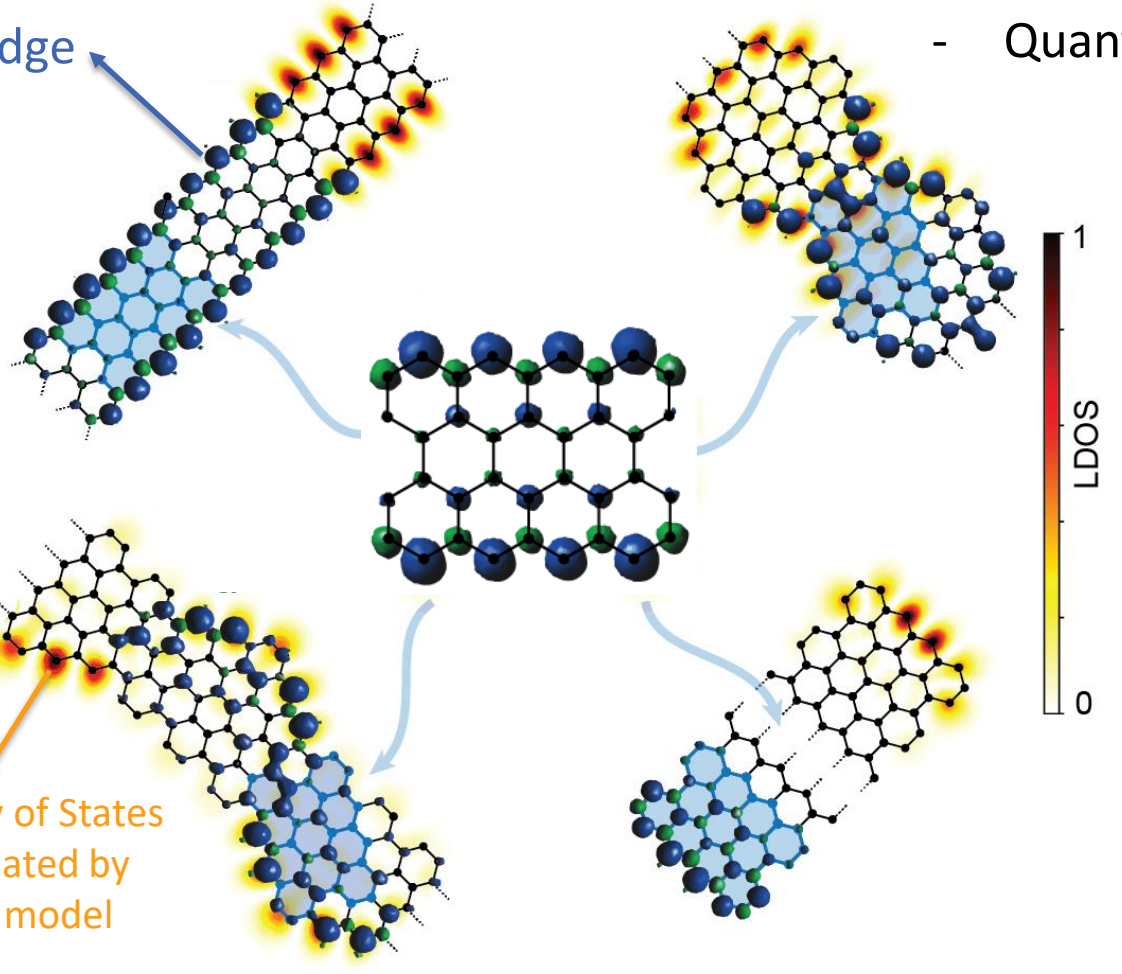


Local Density of States
(LDOS) calculated by
tight binding model

Zigzag Edge in Extended Structures

- Topological phase
- Quantum spin chain

Spin-polarized states in zigzag edge

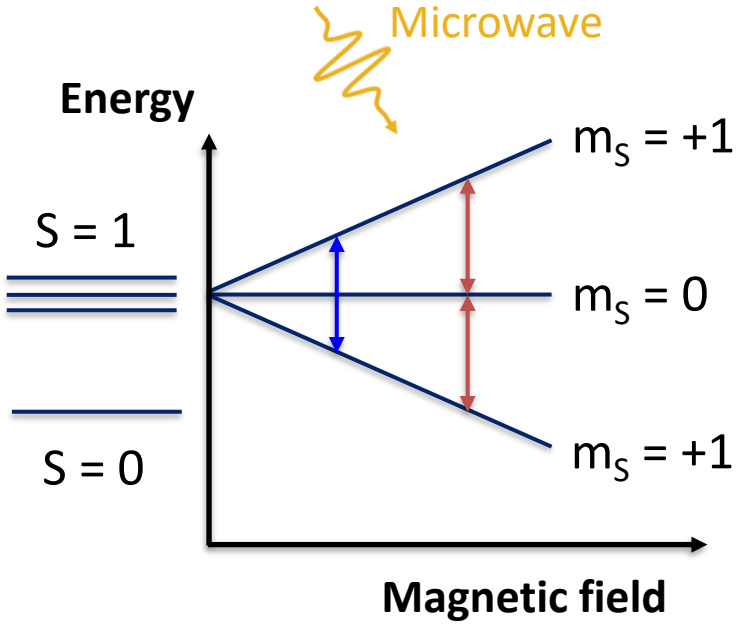


Local Density of States (LDOS) calculated by tight binding model

CW EPR Spectrum of Peri-tetracene

CW EPR:

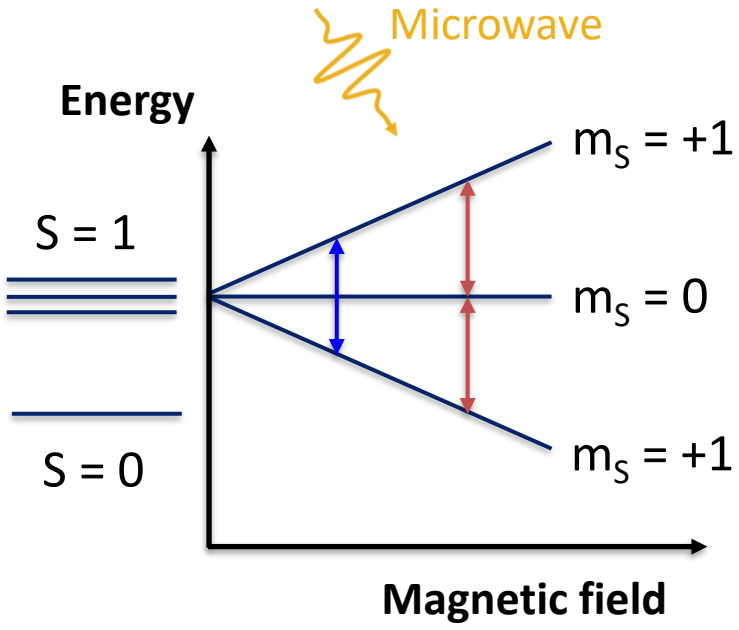
Continuous Wave Electron Paramagnetic Resonance

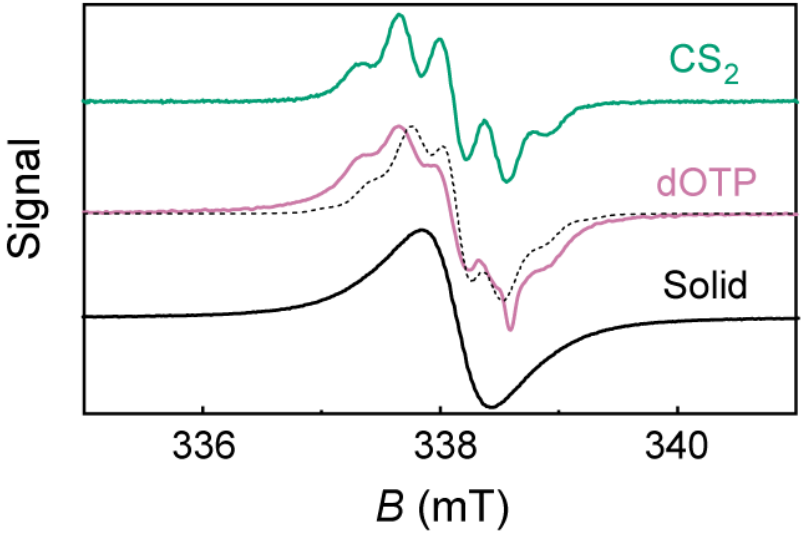


CW EPR Spectrum of Peri-tetracene

CW EPR:

Continuous Wave Electron Paramagnetic Resonance

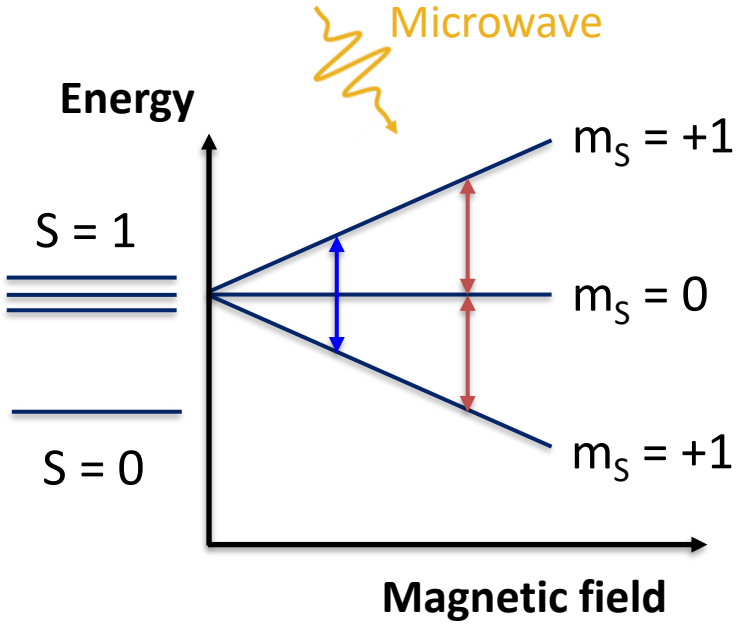


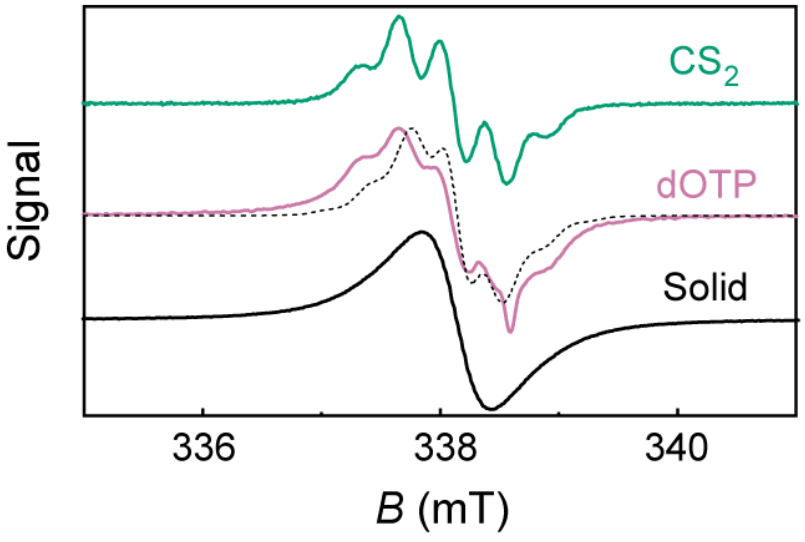


CW EPR Spectrum of Peri-tetracene

CW EPR:

Continuous Wave Electron Paramagnetic Resonance





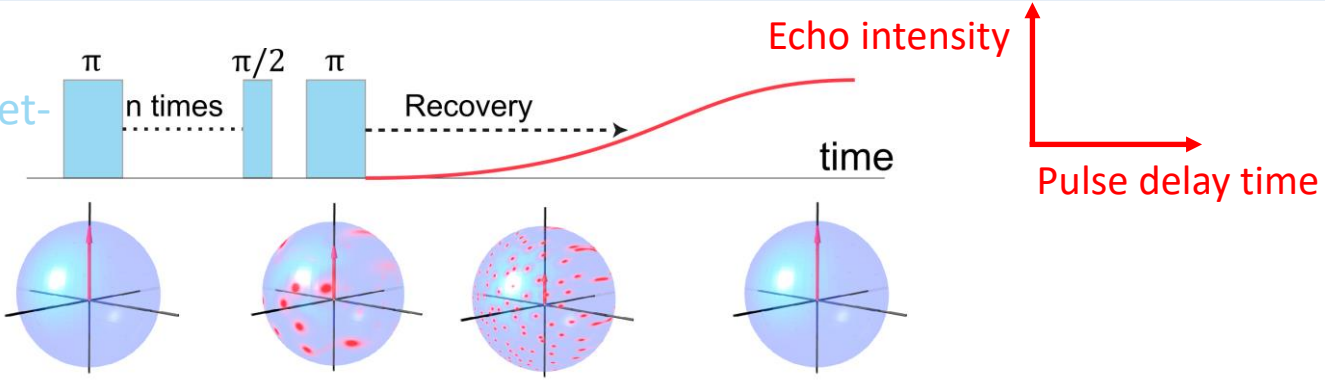
Hamiltonian to describe the system:

$$\hat{H} = \mu_B \boldsymbol{B} \cdot \boldsymbol{g} \cdot \hat{\boldsymbol{S}} + \sum_i^8 \hat{\boldsymbol{S}} \cdot \boldsymbol{A}_i \cdot \hat{\boldsymbol{I}}_i$$

Zeeman energy Hyperfine interaction

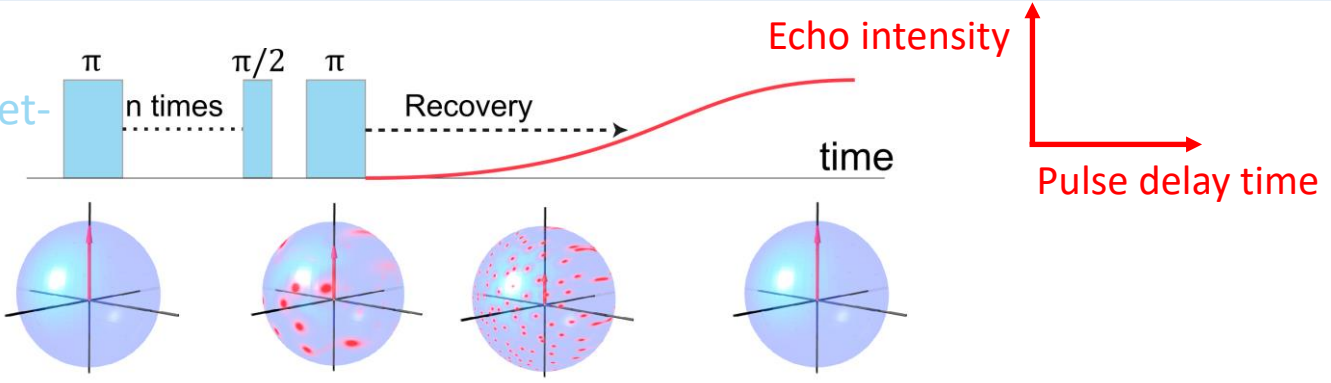
Pulsed EPR Study: Spin-Lattice Relaxation

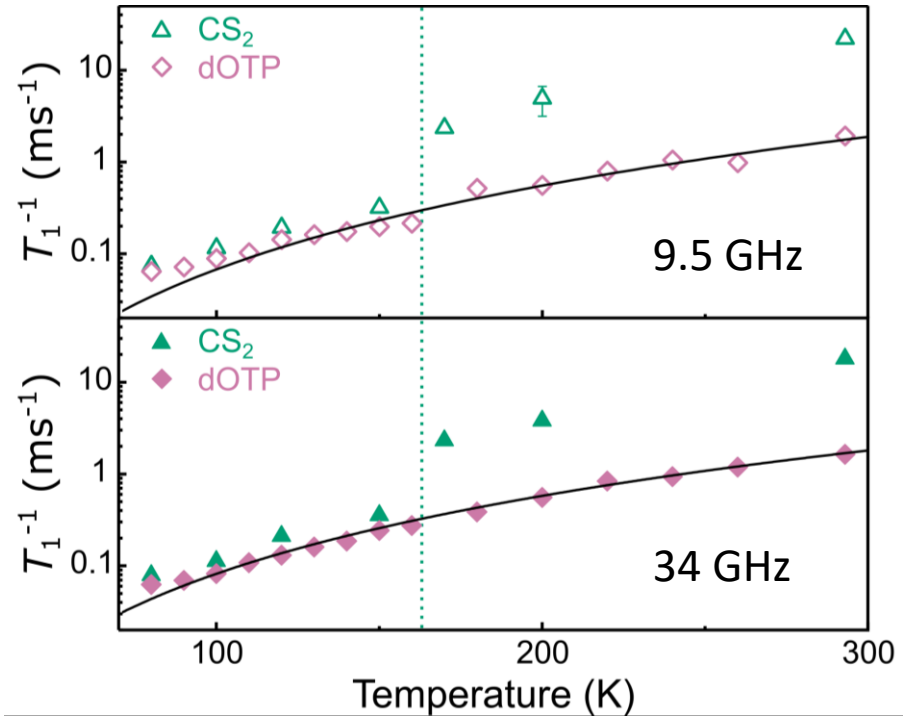
Measure T_1 by picket-fence sequence



Pulsed EPR Study: Spin-Lattice Relaxation

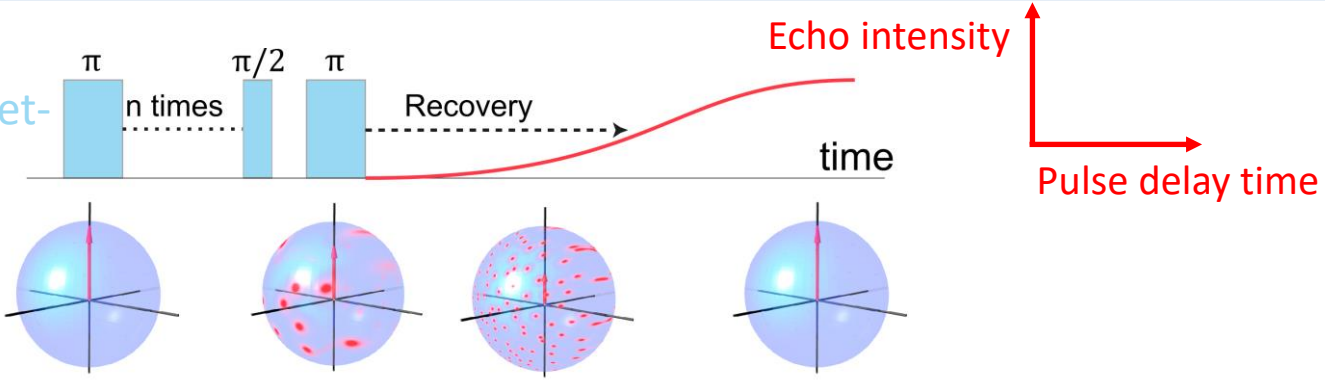
Measure T_1 by picket-fence sequence

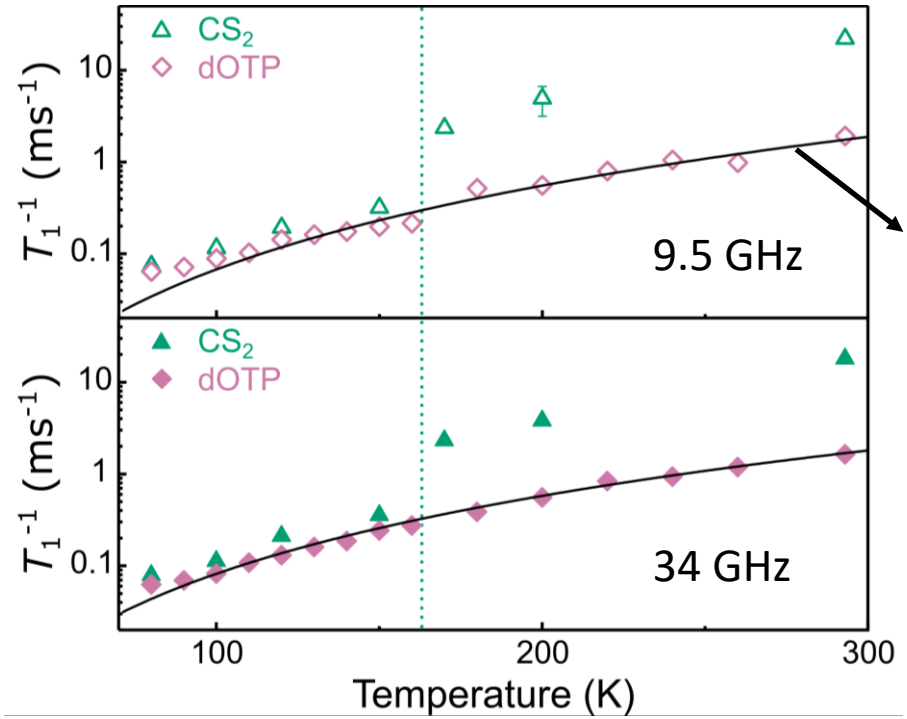




Pulsed EPR Study: Spin-Lattice Relaxation

Measure T_1 by picket-fence sequence

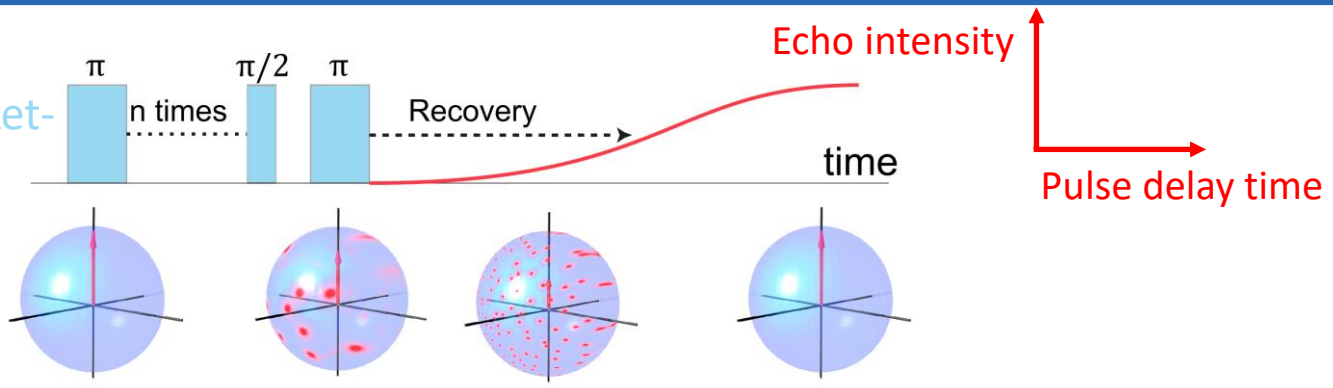




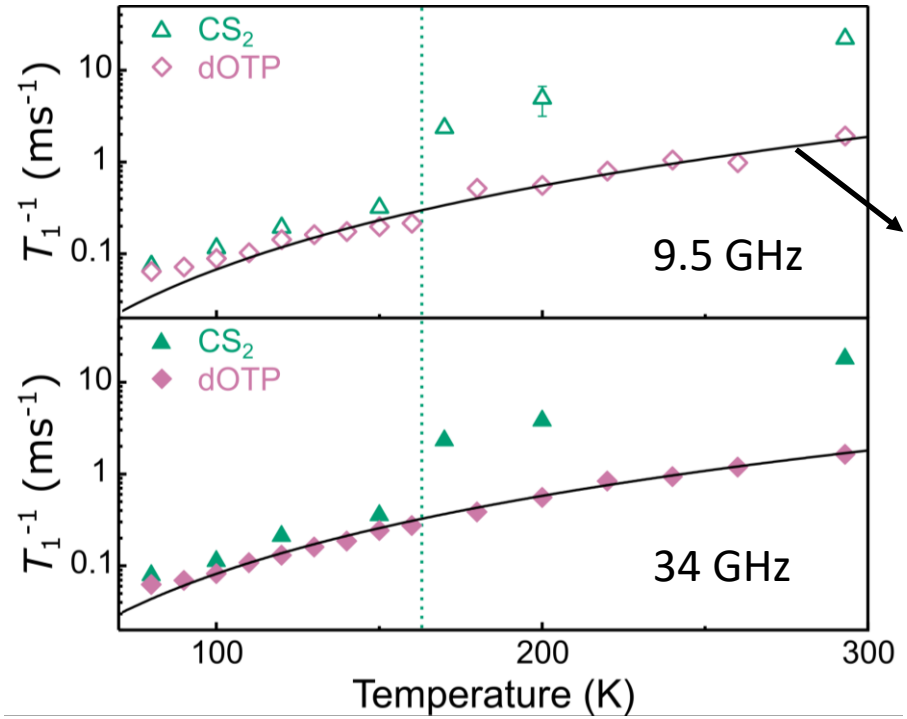
T_1^{-1} vs. T is fitted by direct and Raman relaxation processes

Pulsed EPR Study: Spin-Lattice Relaxation

Measure T_1 by picket-fence sequence

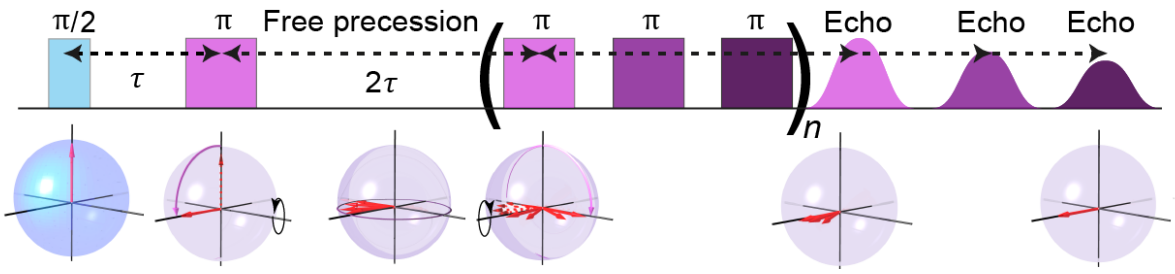


T_1 reaches 0.6-15 ms for T > 80 K in dOTP solution



T_1^{-1} vs. T is fitted by direct and Raman relaxation processes

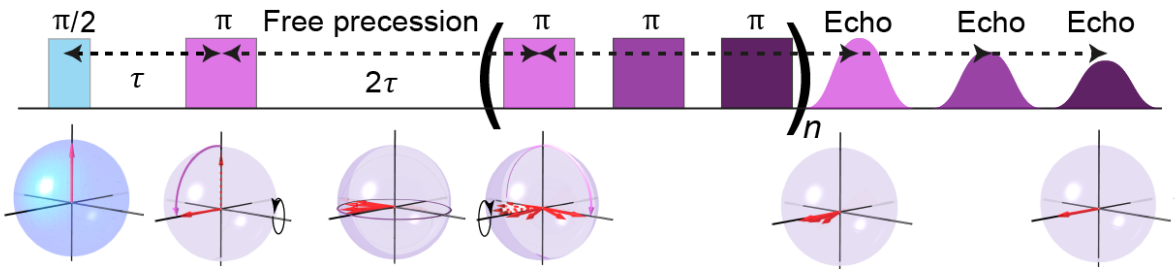
Spin Coherence



Carr-Purcell-Meiboom-Gill (CPMG) sequence

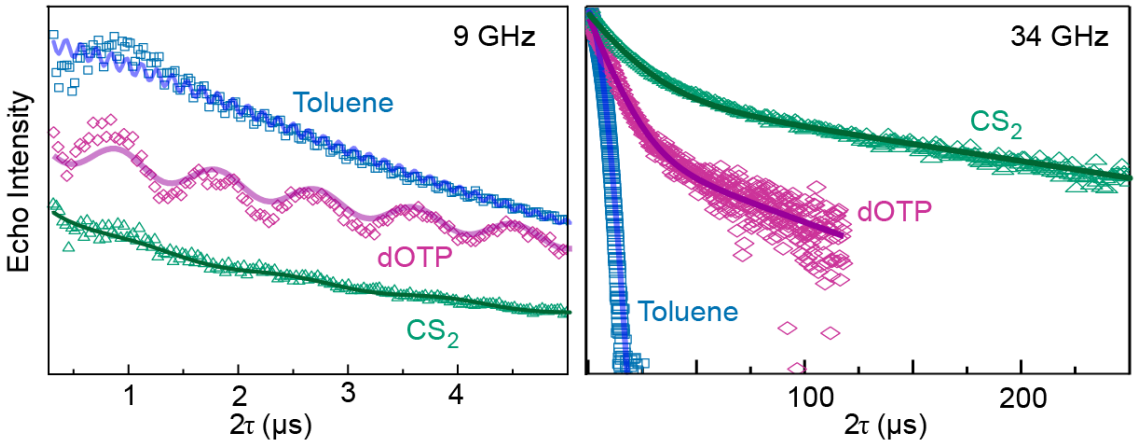
($n = 1$: Hahn echo)

Spin Coherence



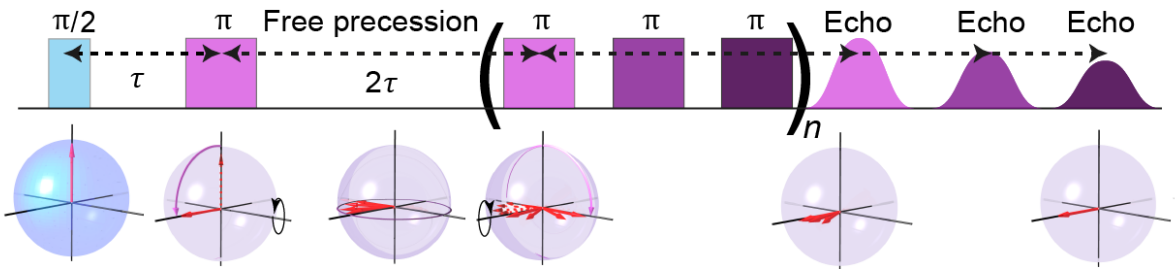
Carr-Purcell-Meiboom-Gill (CPMG) sequence

($n = 1$: Hahn echo)



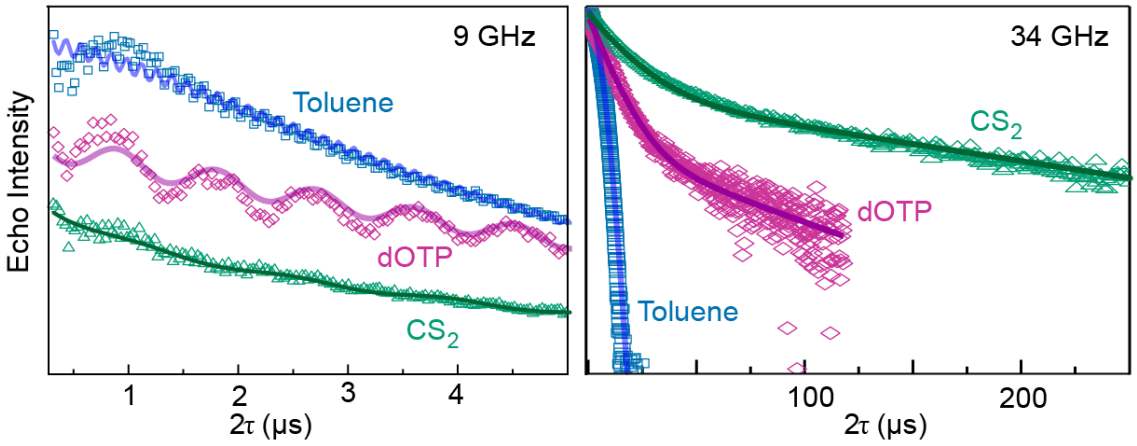
Echo decay with nuclear modulation effect

Spin Coherence

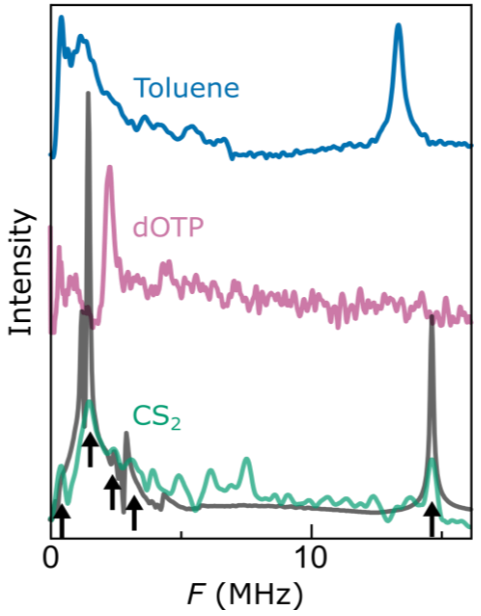


Carr-Purcell-Meiboom-Gill (CPMG) sequence

($n = 1$: Hahn echo)



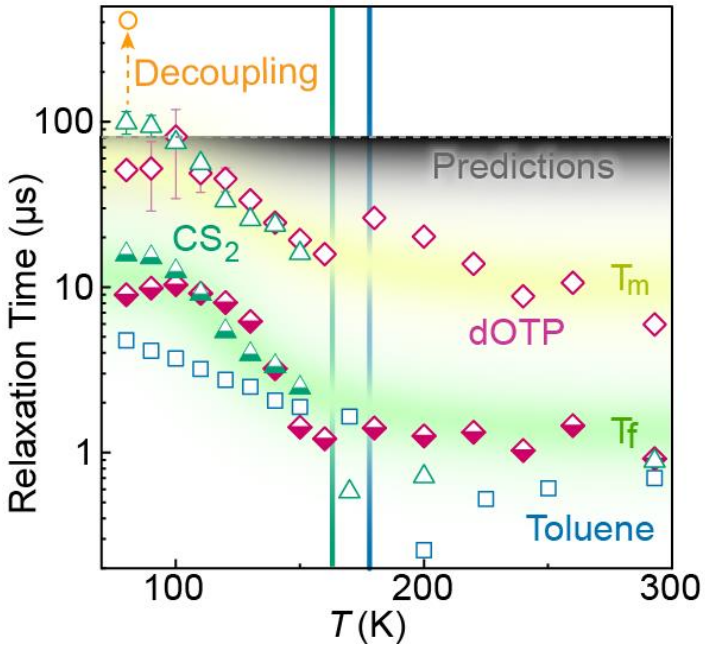
Echo decay with nuclear modulation effect



Fourier transform

Spin Coherence

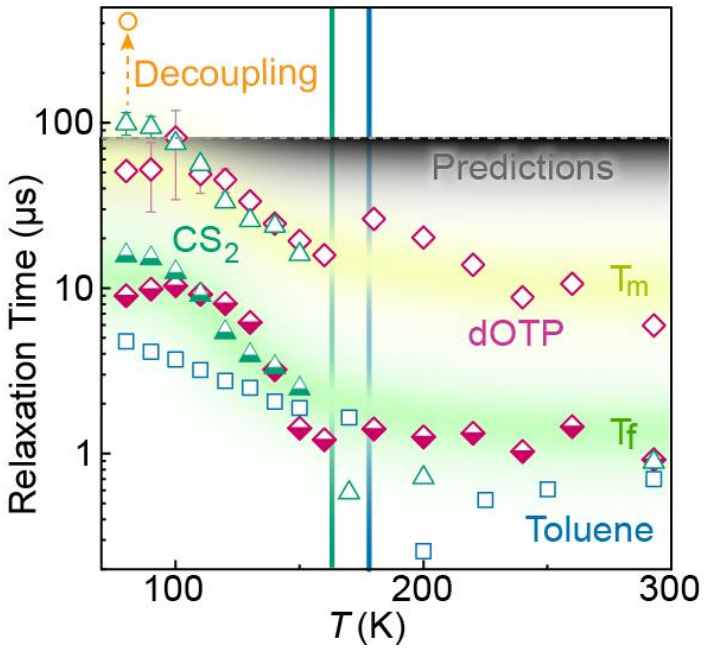
Coherence time T_m and fast relaxation time constant T_f from bi-exponential fitting

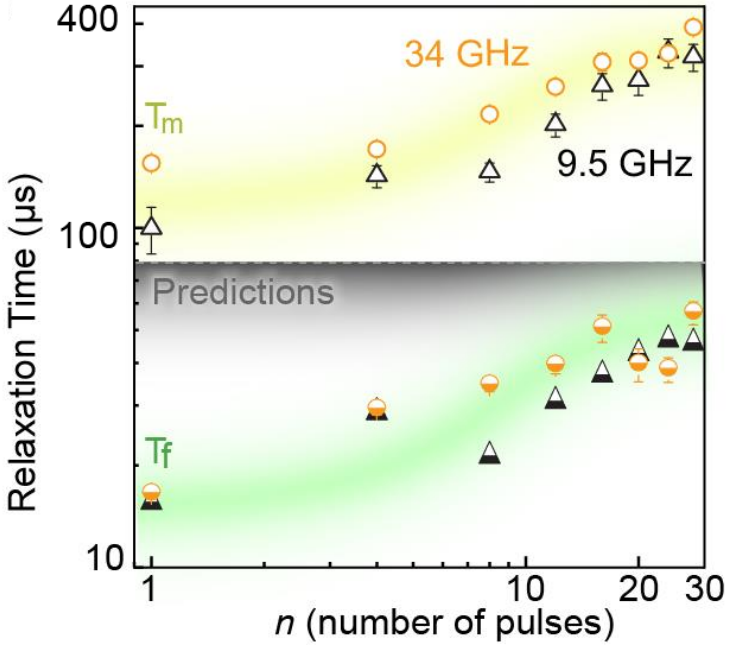


T_m reaches **100 μs** at 80 K in CS2,
exceeding theoretical predictions

Spin Coherence

Coherence time T_m and fast relaxation time constant T_f from bi-exponential fitting





T_m reaches **100 μs** at 80 K in CS2, **exceeding theoretical predictions**

Further increasing coherence time up to **400 μs** by **dynamical decoupling** from the nuclear bath

Conclusion

- Short zigzag segment in molecular nanographene as a gateway to understand extended systems.
- Spin coherence time exceeding theoretical predictions.
- More possibilities to build extended graphene nanoribbon systems, which can form quantum spin chain or host topological non-trivial phase.

Acknowledgements

University of Oxford

Lapo Bogani
Federico Lombardi
Michael Slota
Karen Yan
William Myers

NUS

Yong Ni
Jishan Wu