Molecular Magnetism

Theory & Experiment

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DIPC Community Seminar – March 16th 23

Outline

- Motivation
- Molecular Magnetism
  - Experimental characterisation
  - Theory and computation
- Single Molecule Magnets
  - What makes an SMMs and why do we focus on Dy(III)?
  - Molecular design: from static to dynamic properties
- Organic Radicals
  - How to trick metal-free molecules into not forming bonds: topology
  - Impact of structural flexibility
- What's next?

Outline

- Motivation

- Molecular Magnetism
  - Experimental characterisation
  - Theory and computation

~ 20 minutes

- Single Molecule Magnets
  - What makes an SMMs and why do we focus on Dy(III)?
  - Molecular design: from static to dynamic properties

~ 10 minutes

- Organic Radicals
  - How to trick metal-free molecules into not forming bonds: topology
  - Impact of structural flexibility

~ 10 minutes

- What's next?

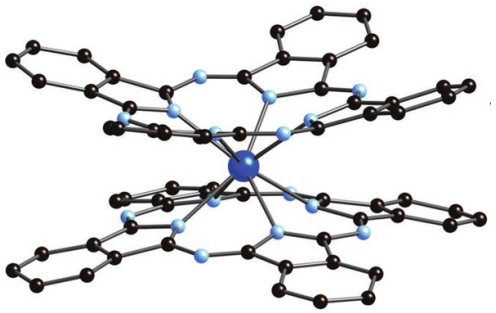
~ 5 minutes

Motivation

- *Quantum information*

Grover algorithm in a $^{159}Tb(III)Pc_2$
qu*d*it single molecule transistor

a)



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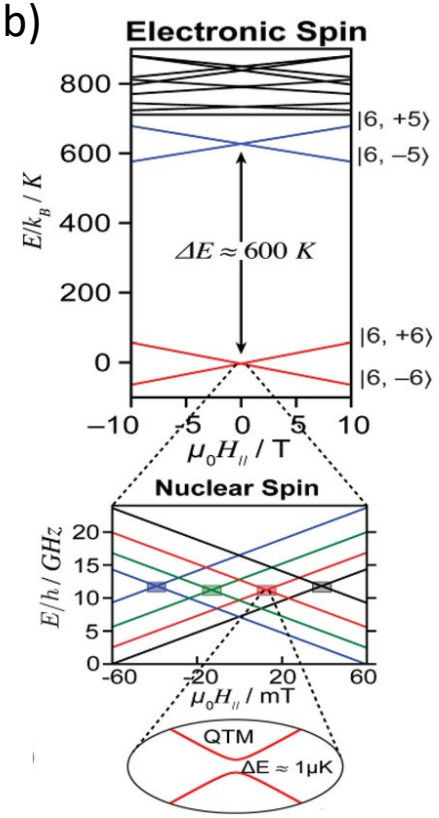

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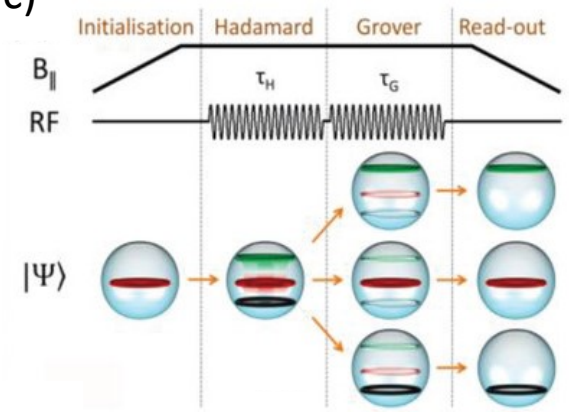
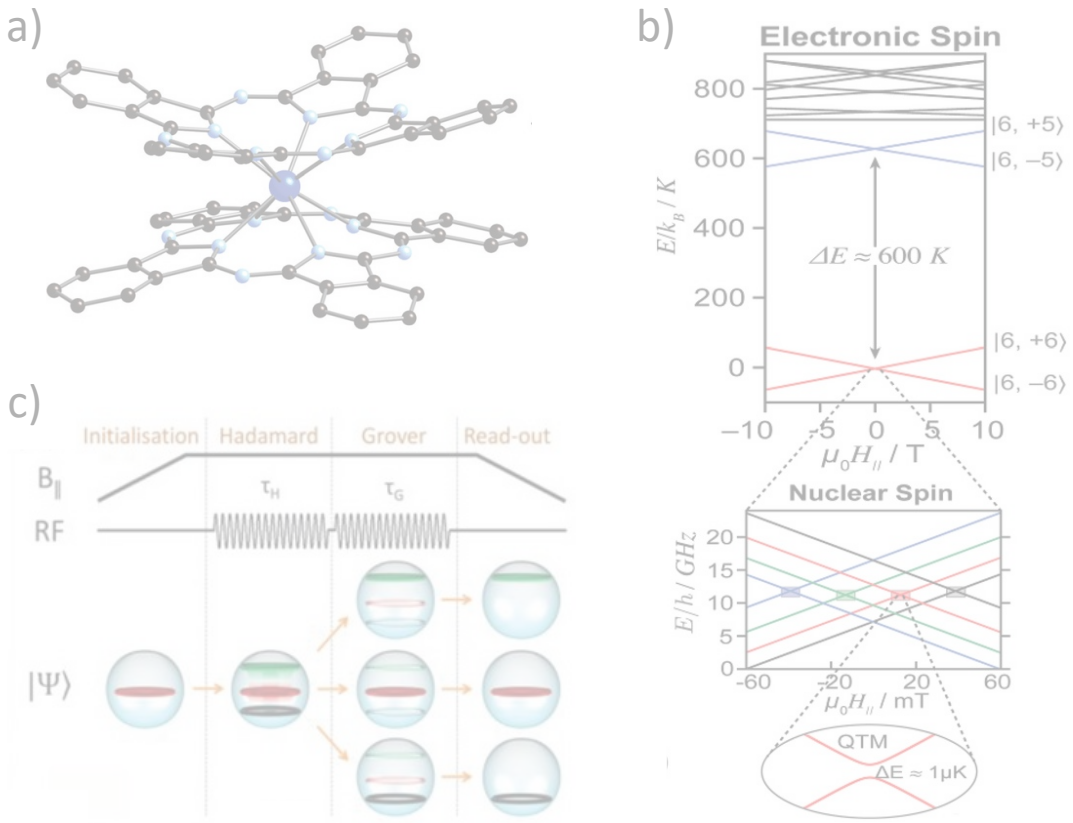


Chem. Soc. Rev., **2012**, *41*, 7464-7478
Phys. Rev. Lett. **2017**, *119*, 187702 *Adv. Mater.* **2019**, *31*, 1806687

Motivation

- *Quantum information*

Grover algorithm in a $^{159}Tb(III)Pc_2$ **qu*d*it** single molecule transistor



Chem. Soc. Rev., **2012**, *41*, 7464-7478
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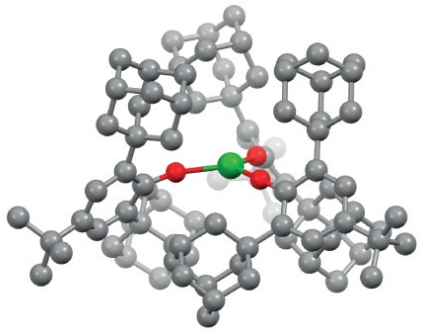
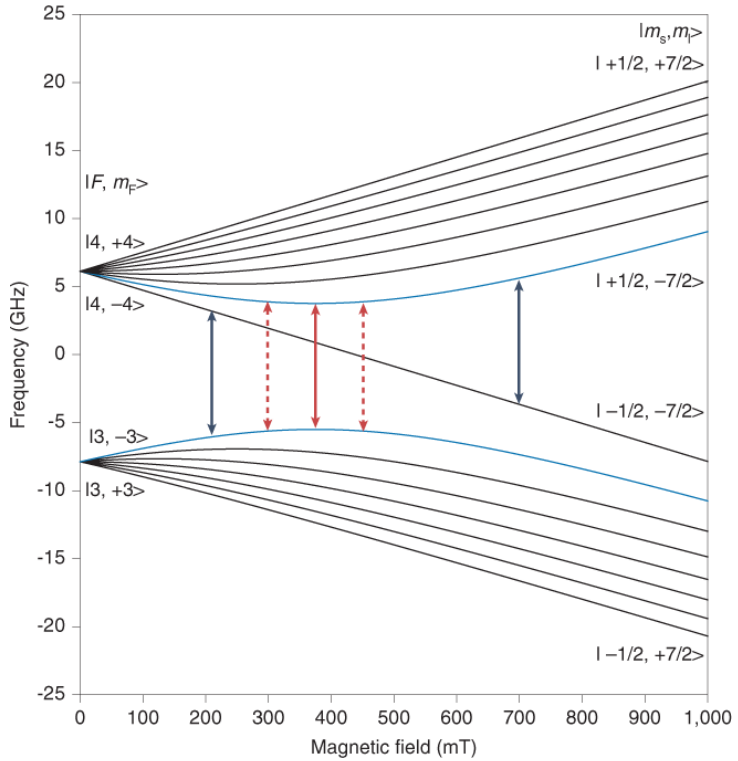
Improving **quantum coherences** by operating at clock transitions (CT) in a Lu(II) $5d^1$



$$\frac{dE}{dB} \propto M$$

At CT, system is protected from magnetic noise (dipolar fields)



$$F = I + S$$
$$E \propto B_0 m_F$$

$$\mu_B \vec{B} \bar{\bar{g}} \vec{\hat{S}}$$
$$E \propto B_0 m_S$$

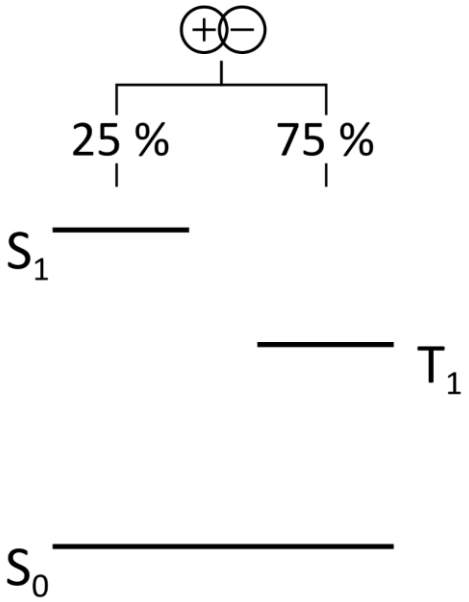
Nat. Chem. **2022**, *14*, 361–362 *Nat. Chem.* **2022**, *14*, 392–397

Motivation

- *OLEDs*

Spin-statistics limit Quantum Efficiency

Conventional fluorescence



Chem. Soc. Rev., **2017**, *46*, 915-1016

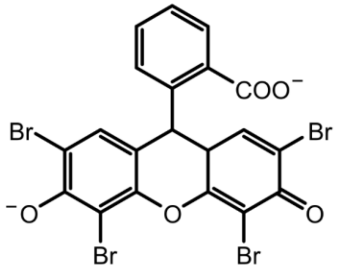
Motivation

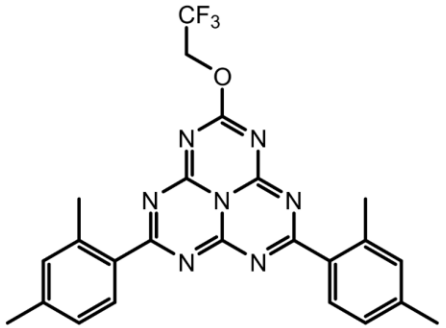
- *OLEDs*

Improving Quantum Efficiency →

Spin-statistics limit Quantum Efficiency

Involve T_1 (ΔE_{ST} & SOC) to improve QE



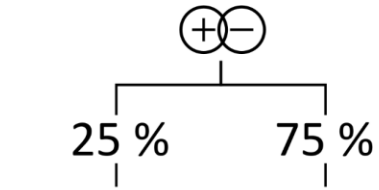


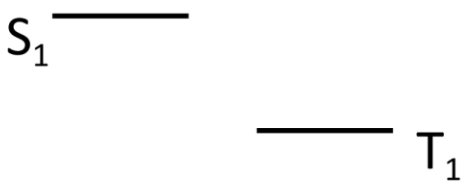
Conventional fluorescence

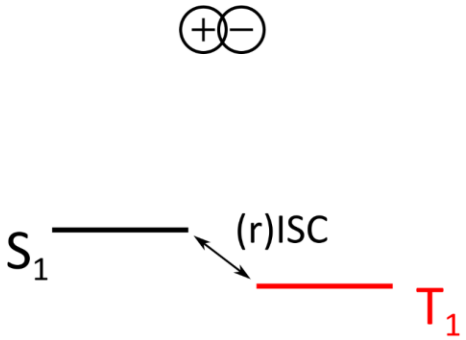
TADF

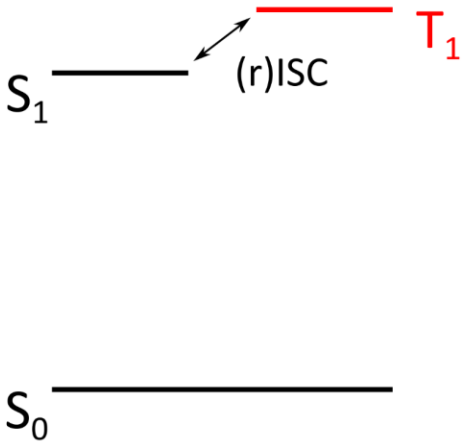
DFIST

17%









Chem. Soc. Rev., **2017**, *46*, 915-1016

Nature, **2022**, *609*, 502–506

Motivation

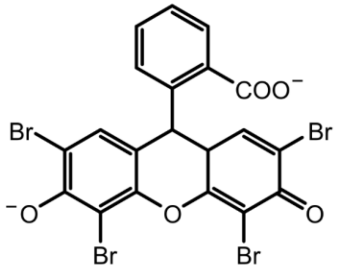
- *OLEDs*

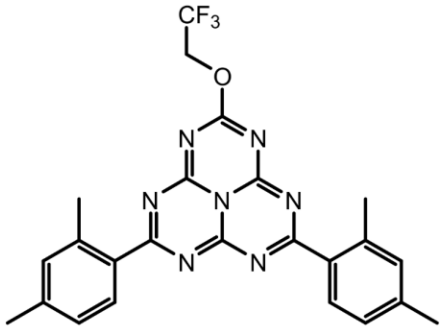
Spin-statistics limit Quantum Efficiency

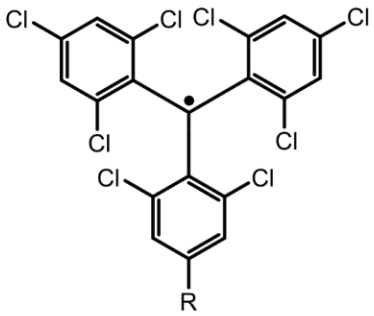
Involve T_1 (ΔE_{ST} & SOC) to improve QE

Spin doublet avoids them altogether

Improving Quantum Efficiency







Conventional fluorescence

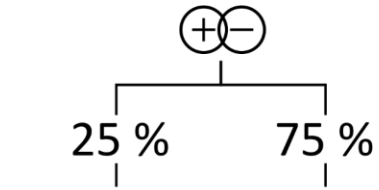
TADF

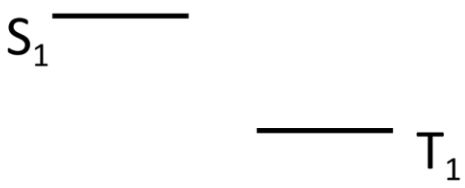
DFIST

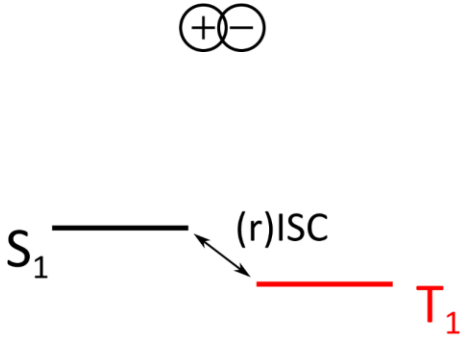
17%

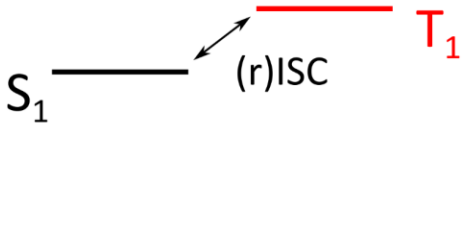
DE

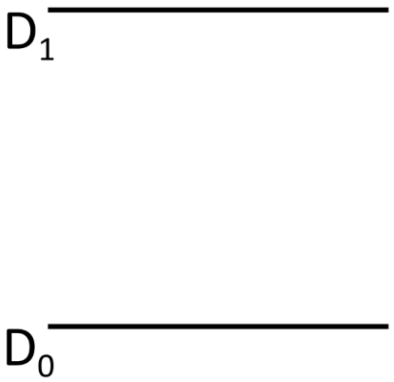
27%











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Nature, **2022**, *609*, 502–506

Nature, **2018**, *563*, 536–540

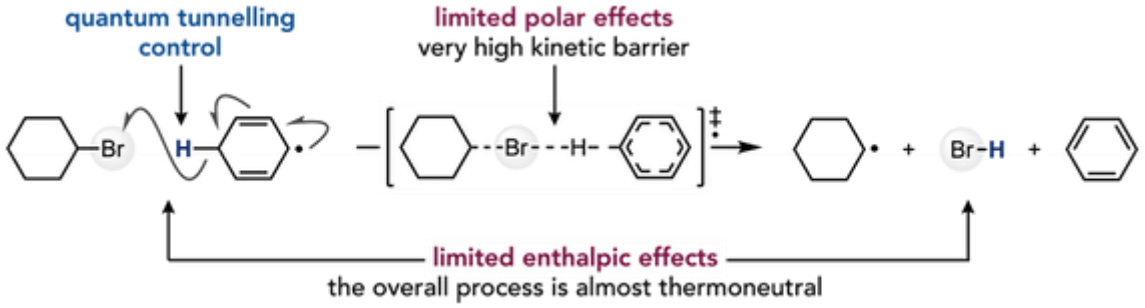
Motivation

- *Synthetic chemistry*

Radical-mediated routes to C-H bond formation

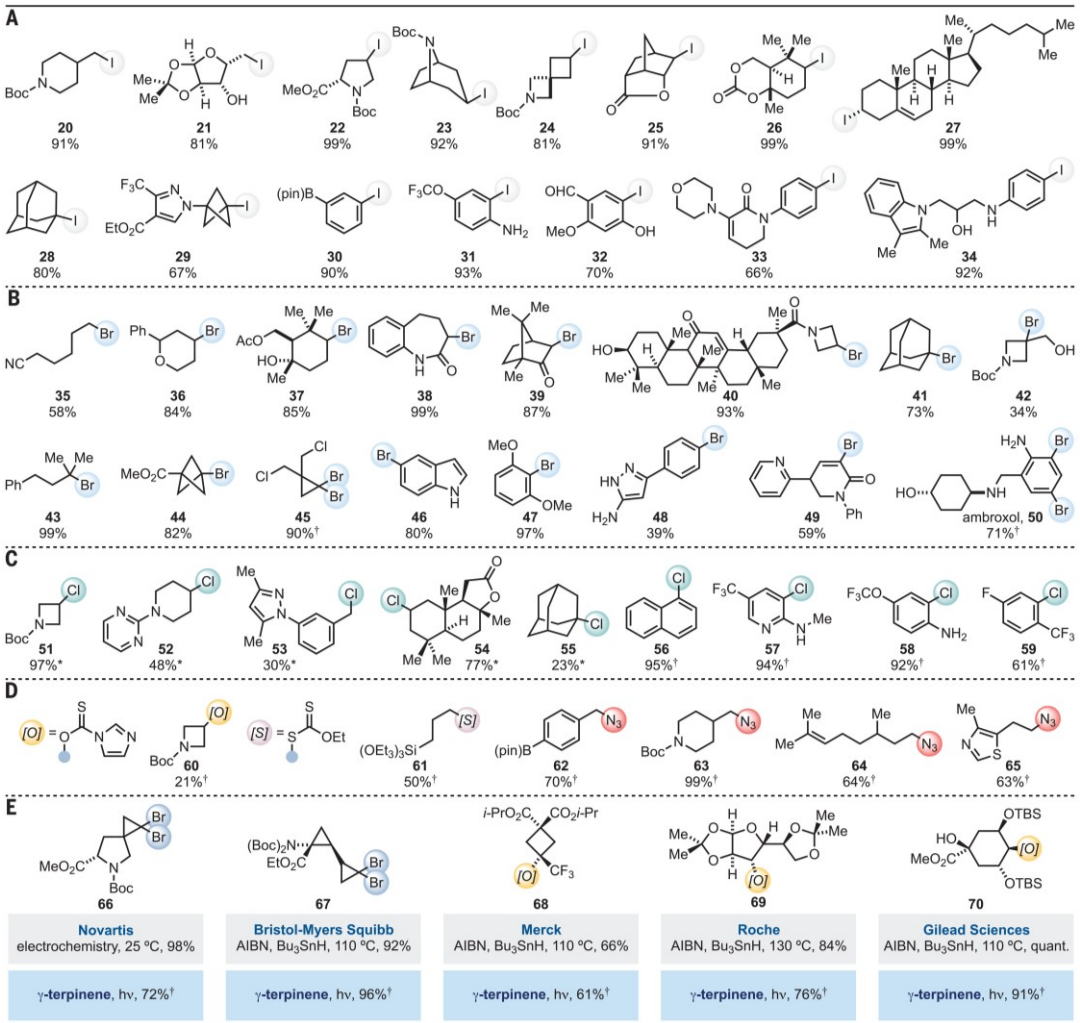
High yields and “mild” conditions

By-product: volatile aromatic in place of tin or silicon waste



Science, **2022**, *377*, 1323–1328

Massive substrate scope

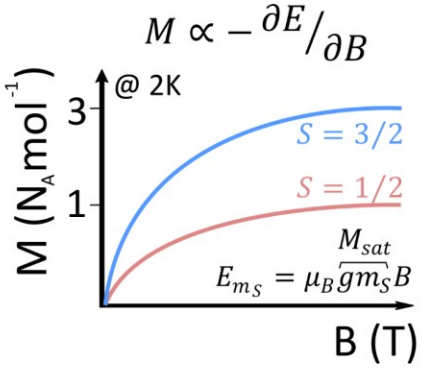


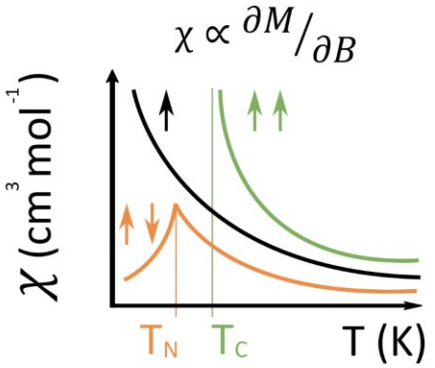
Molecular Magnetism

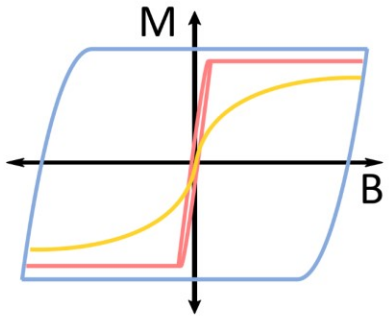
- *Experimental characterisation –*

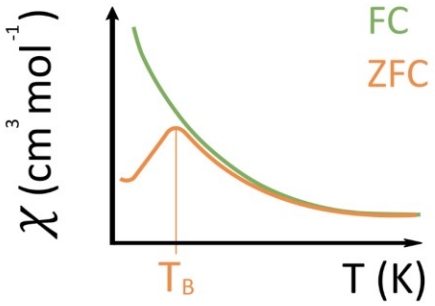
Molecular Magnetism

- *Experimental characterisation* – **DC** magnetometry measures moment varying <u>field</u> and <u>temperature</u>

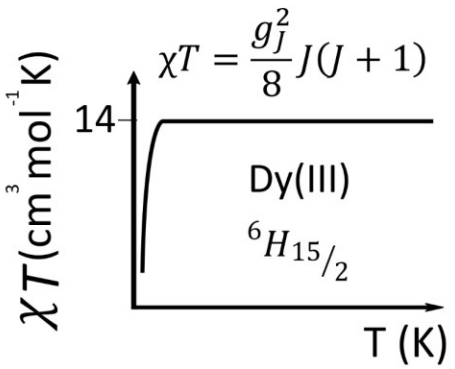






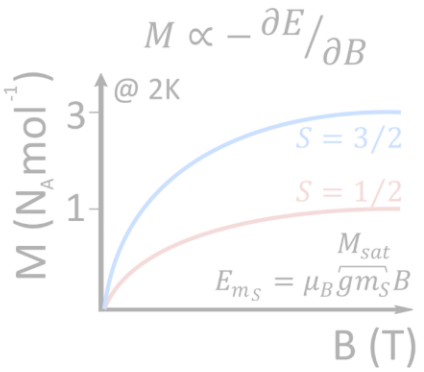


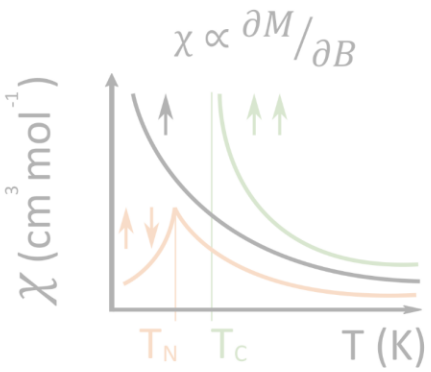
Access to **static** & **dynamic** properties of **spin-only** and **spin-orbit** coupled systems

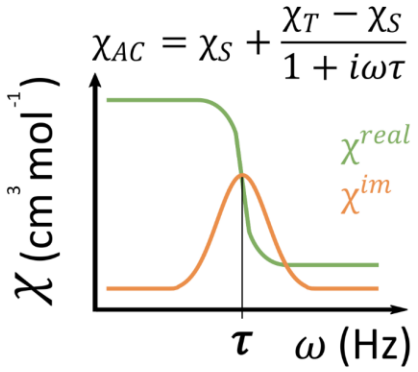


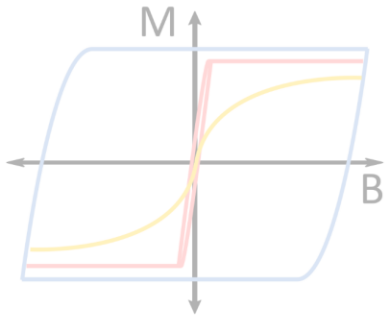
Molecular Magnetism

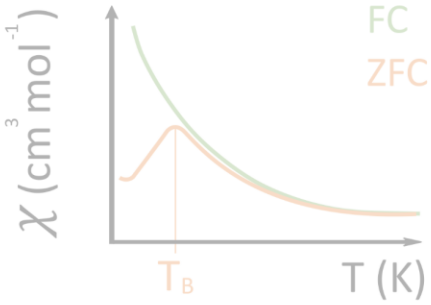
- *Experimental characterisation* – **AC** magnetometry measures moment varying field, temperature and AC frequency

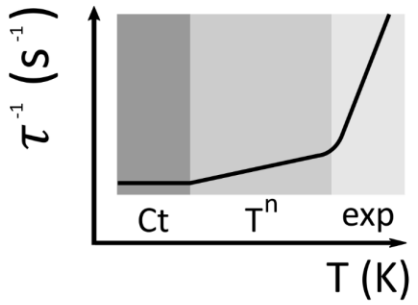




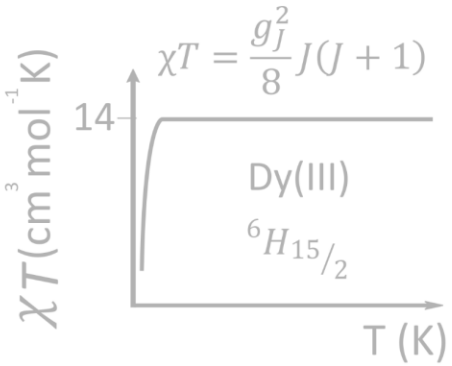








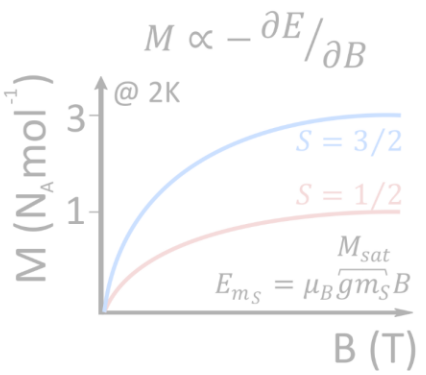
Access to **static** & **dynamic** properties of **spin-only** and **spin-orbit** coupled systems

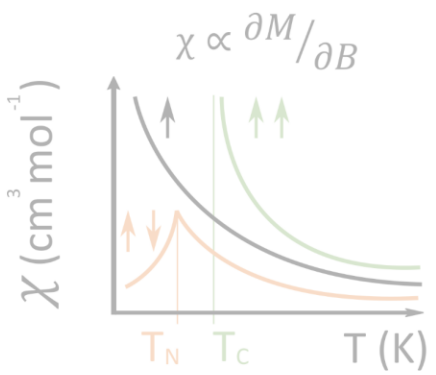


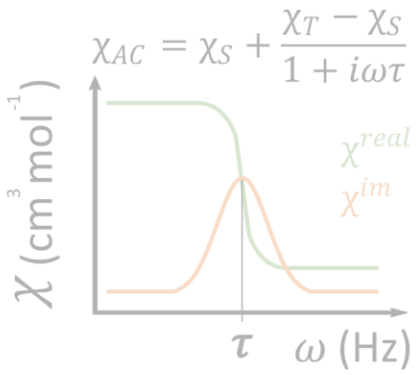
Access to relaxation of magnetisation **characteristic time** (τ)

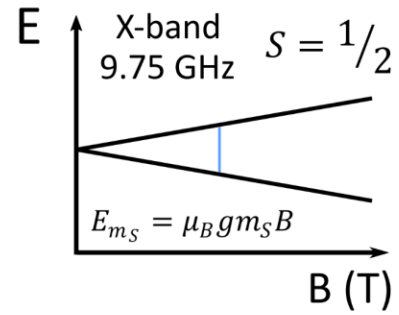
Molecular Magnetism

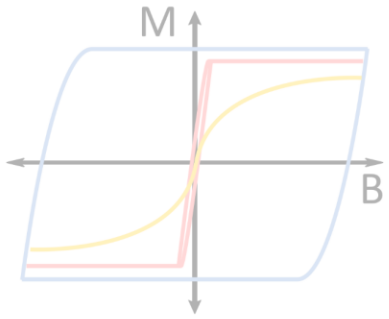
- *Experimental characterisation* – **EPR** measures spin transitions varying <u>field</u> and <u>temperature</u>

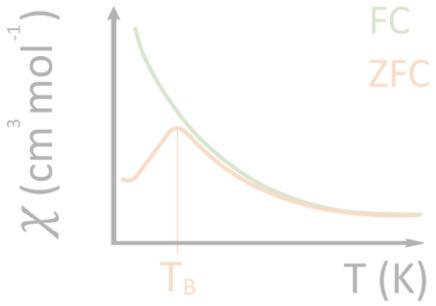


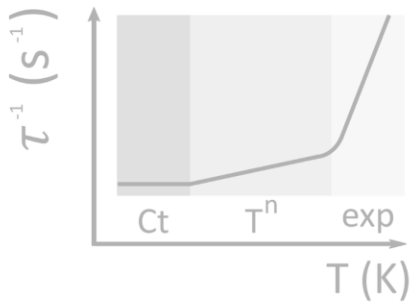


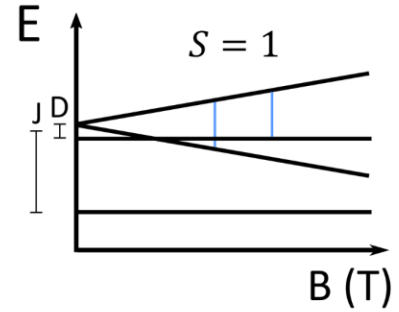




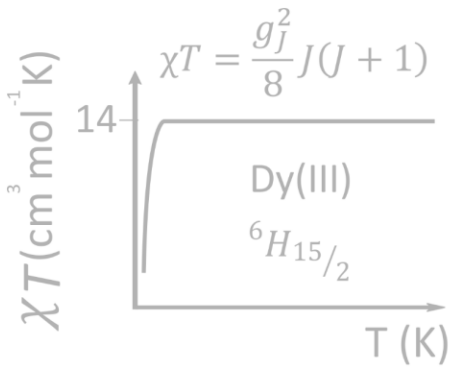




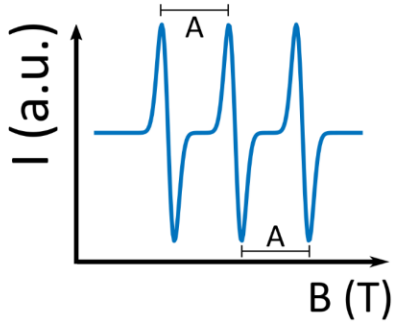




Access to **static** & **dynamic** properties of **spin-only** and **spin-orbit** coupled systems



Access to relaxation of magnetisation **characteristic time** (τ)



Molecular Magnetism

- *Experimental characterisation* – electronic structure interrogated with <u>complementary</u> methods

- A physically meaningful model spin Hamiltonian is formulated for the system
- Data is fitted (global) to validate, refine or discard the model
- Initial guess values are obtained from ab initio methods
- PHI[1] or EasySpin[2] are customarily used

1 J. Comp. Chem., **2013**, *34*, 1164–1175
2 *J. Magn. Reson.* **2006**, *178(1)*, 42-55

Access to **static** & **dynamic** properties of **spin-only** and **spin-orbit** coupled systems

magnetisation **characteristic time** (τ)

Molecular Magnetism

- *Theory and computation –*

Molecular Magnetism

- *Theory and computation* – **Geometry optimisation** with Density Functional Theory (DFT)

  - Both in gas-phase (*Gaussian*) and periodic conditions (*Crystal, VASP, Phonopy*)
  - For spin-only systems:
    - Hybrid, GGA, meta-GGA, range-corrected functionals & standard basis sets
  - For spin-orbit coupled systems:
    - Exchange-correlation functionals & ECPs – diamagnetic analogue with actual isotopic mass for normal modes

Molecular Magnetism

- *Theory and computation* – **Electronic structure** with DFT & multiconfigurational methods (CASSCF, PT2, MRCI)

  - For spin-only systems:

    - ΔE between spin-adapted (*OpenMolcas*) states describe model spin Hamiltonian parameters (J, ZFS, $^{t}/_{U}$, ⋯)
    - Mapping approaches to employ broken symmetry solutions (*Gaussian*)
    - Standard basis sets

Exact

$$\hat{H}_{elec} = -\sum_{i=1}^{N} \tfrac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>1}^{N} \frac{1}{r_{ij}}$$

Non-relativistic & time-independent

Spin-adapted

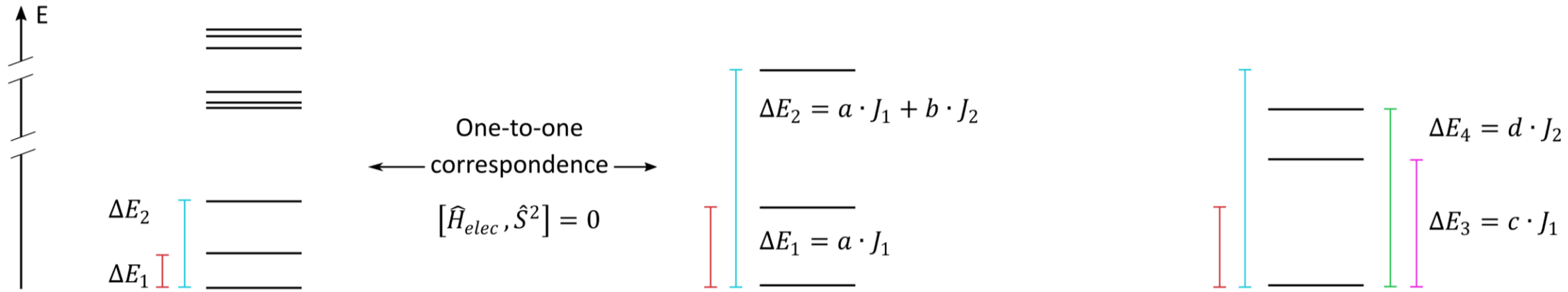
$$\hat{H}^{HDVV} = -\sum_{\langle i,j \rangle} J_{ij}\hat{S}_i \cdot \hat{S}_j$$

$$|\Psi\rangle_{MC} = \sum_I c_I |\phi_I\rangle$$

broken-symmetry

$$\hat{H}^{Ising} = -\sum_{\langle i,j \rangle} J_{ij}\hat{S}_i{}^{z} \cdot \hat{S}_j{}^{z}$$

$$|\Psi\rangle_{BS} = |\phi\rangle$$



Molecular Magnetism

- *Theory and computation* – **Electronic structure** with DFT & multiconfigurational methods (CASSCF, PT2, MRCI)

  - For spin-only systems:
    - ΔE between spin-adapted (*OpenMolcas*) states describe model spin Hamiltonian parameters (J, ZFS, $^{t}/_{U}$, $\cdots$)
    - Mapping approaches to employ broken symmetry solutions (*Gaussian*)
    - Standard basis sets

  - For spin-orbit coupled systems (*OpenMolcas*) :
    - Relativistic corrections: scalar 2nd-order Douglas-Kroll-Hess and ANO-RCC basis set
    - SOC: AMFI and State-Interaction between appropriate number of states for each spin-multiplicity
    - Parametrisation of ab initio results by means of Crystal Field Theory

$$\hat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^{k} {B_k}^q \theta_k {\hat{O}_k}^q$$

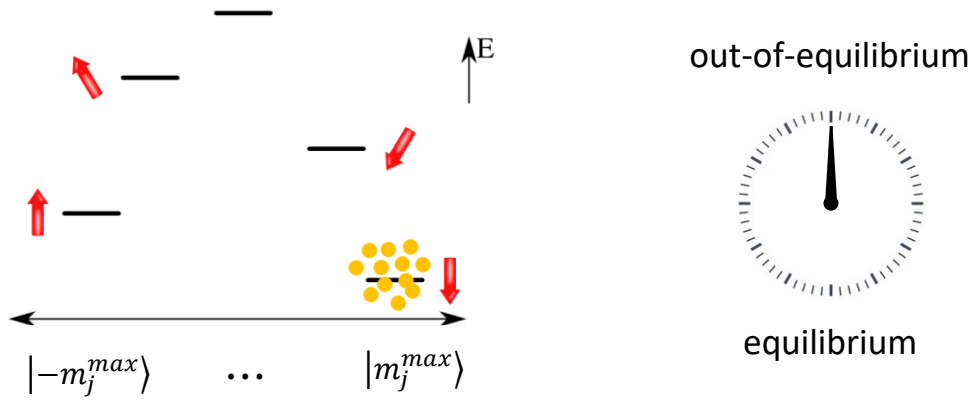
${B_k}^q$: Crystal Field Parameters (CFPs)
θ_k: Operator equivalent factors
${\hat{O}_k}^q$: Stevens operators (LC of $\hat{L}_Z$, $\hat{L}_+$, $\hat{L}_-$)

Molecular Magnetism

- *Theory and computation* – **Spin dynamics** with master matrix & 1st order TDPT

  - Description of spin-phonon coupling:
    - Gas-phase molecular normal modes
    - Transition rates are calculated with Fermi's golden rule
    - Orbach process

  - Dynamics:
    - Master matrix formalism
    - Solution yields how long it takes to reach equilibrium τ
    - Solve at different temperatures for direct comparison to experimental relaxation profiles
    - Identify main deactivation pathways and *hope* to affect them with molecular design



Single Molecule Magnets

- *What makes an SMM and why Dy(III)?*

  Slow relaxation of magnetisation → roughly $10^5 < \tau(s) < 10^2$ at 2 K, $\tau(s) < 10^{-4}$ as hot as possible

  - Key ingredient is magnetic anisotropy, achieved with large spin-orbit coupling (SOC)

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Example: Dy(III) $4f^9$ electronic configuration. 4*f* orbitals are shielded by filled atomic shells → unquenched L

m_L : -3 -2 -1 0 1 2 3 $\qquad L = \sum m_L = 5$

m_S : 0 0 $^1/_2$ $^1/_2$ $^1/_2$ $^1/_2$ $^1/_2$ $\qquad S = \sum m_S = {}^5/_2$

Russell-Saunders coupling scheme: $\quad |L - S| \leq J \leq |L + S|$

$$^5/_2 \leq J \leq {}^{15}/_2$$

How are they distributed?

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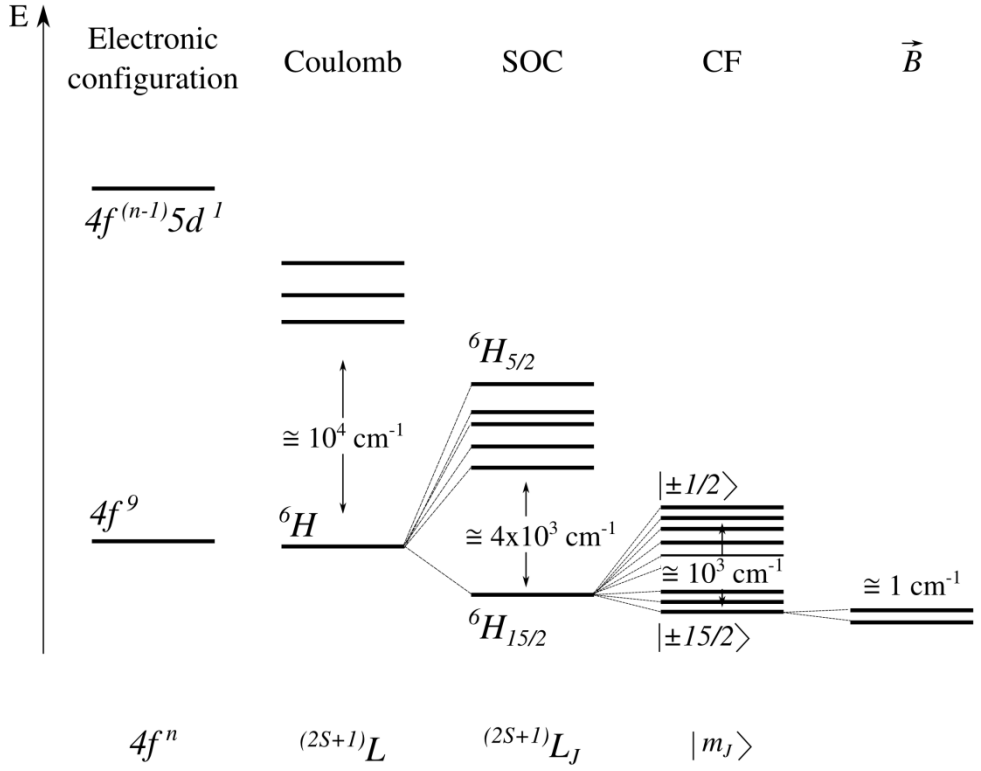

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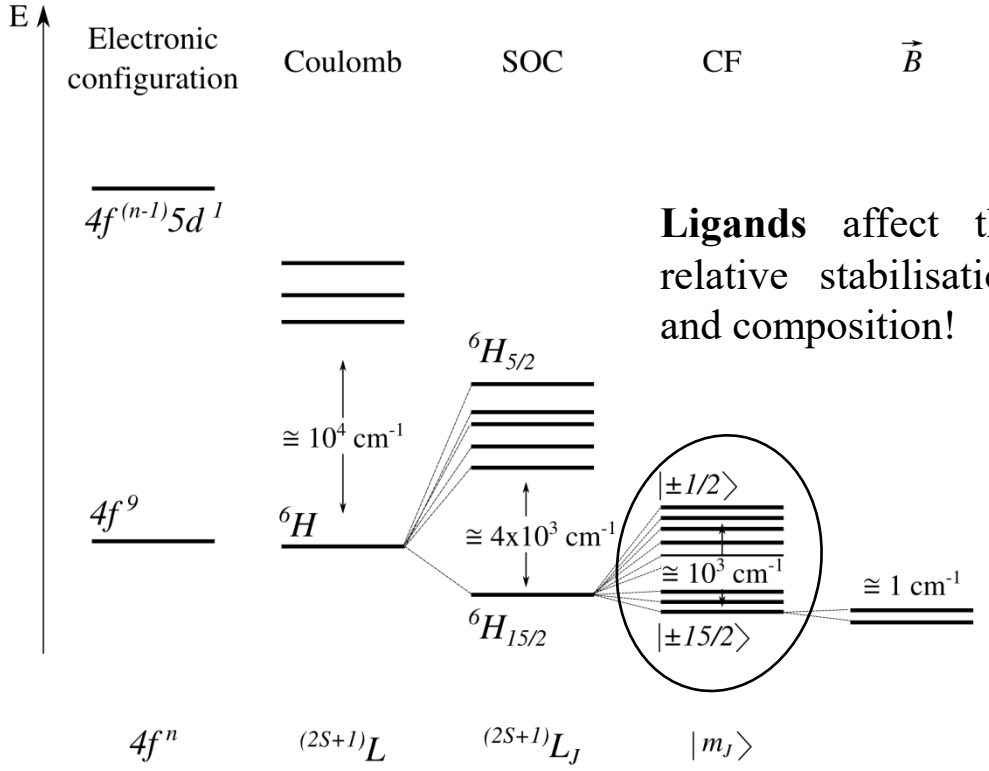

Ligands affect the relative stabilisation and composition!

Single Molecule Magnets

- *Molecular design: from static to dynamic properties*

Axial ligand fields are key

  - ➢ States with largest m_J are <u>stabilised</u>; states with smallest m_J are <u>destabilised</u> – ΔE informs of U^{eff}

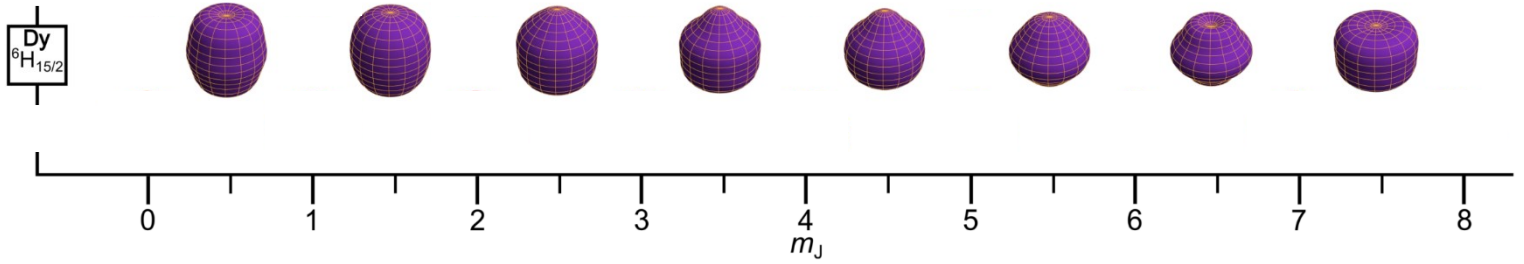

Fig. Free-ion charge density plots for the m_J states of the ground Hund's rule term of Dy(III) as derived by Sievers.[1] Figure credit: J. G. C. Kragskow.

1 J. Sievers, Zeitschrift für Physik B, Condensed Matter **1982**, *45*, 289-296.

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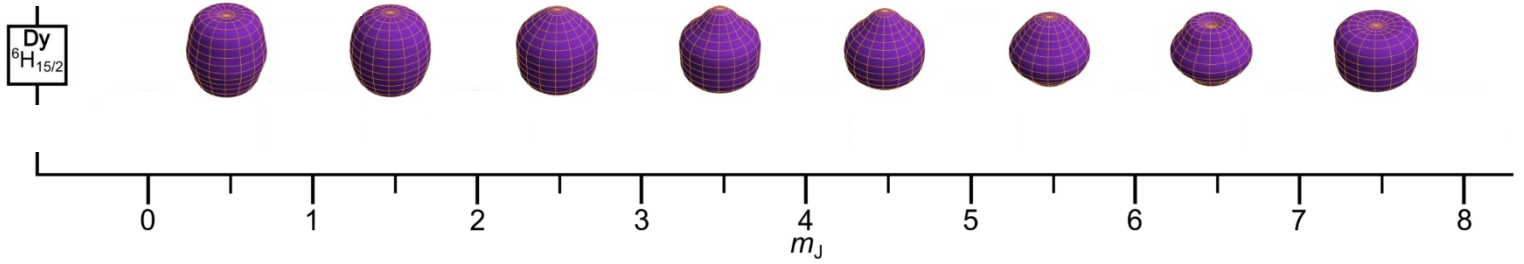

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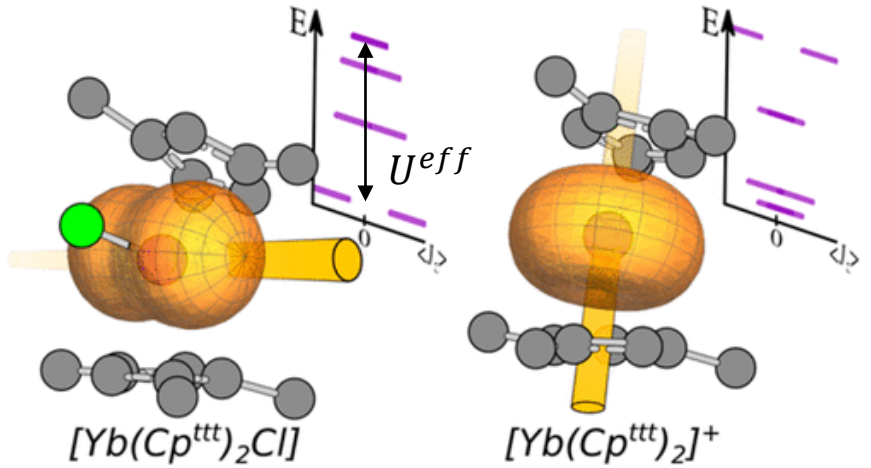
- U^{eff} is a key indicator of a SMM performance (static) – <u>How easy it is to relax over the barrier</u>



Note that for Yb(III), stabilisation is reversed wrt Dy(III)

C. A. P. Goodwin, D. Reta, F. Ortu, N. F. Chilton, D. P. Mills, *JACS* **2017**, *139*, 51, 18714–18724

Single Molecule Magnets

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Cyclopentadienyl-based Dy(III) are the best performing SMMs

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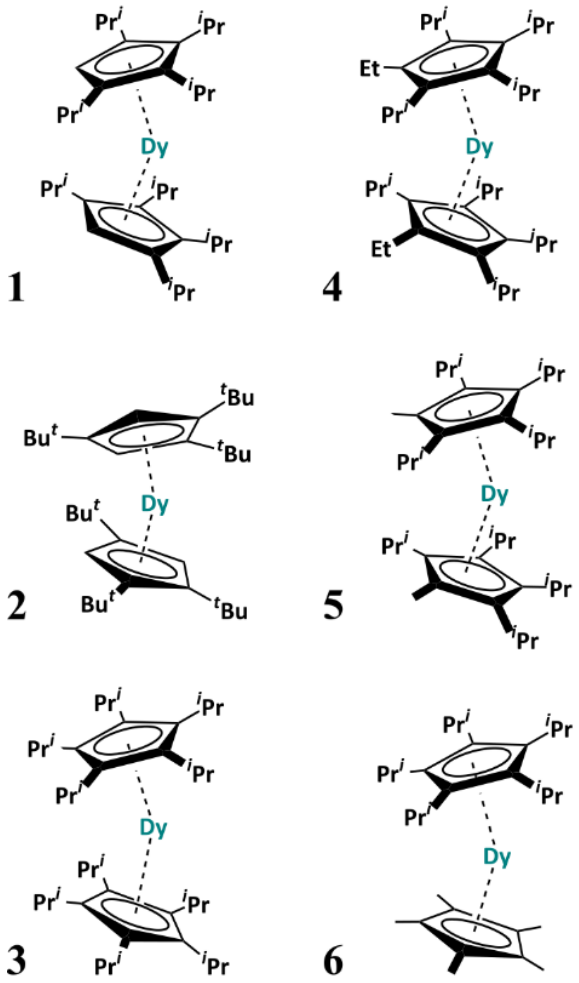

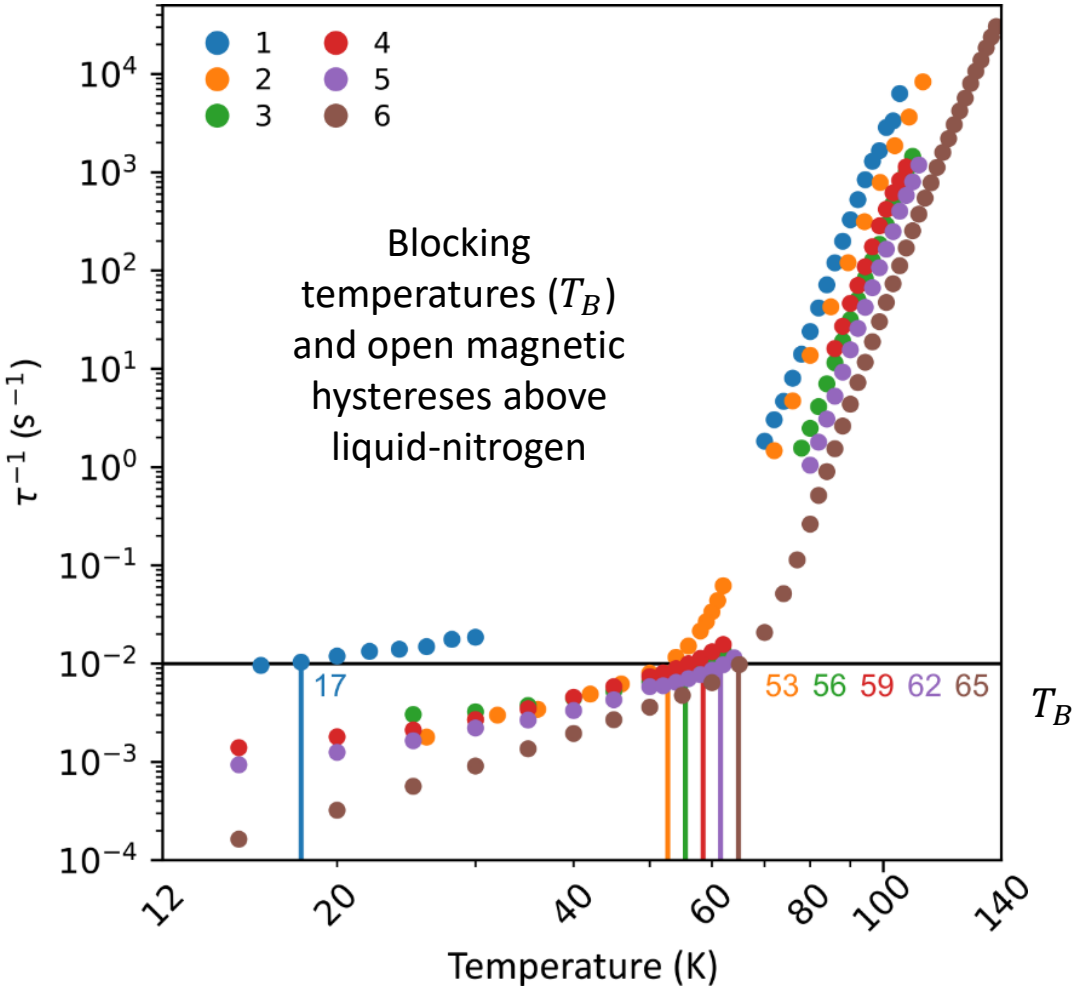

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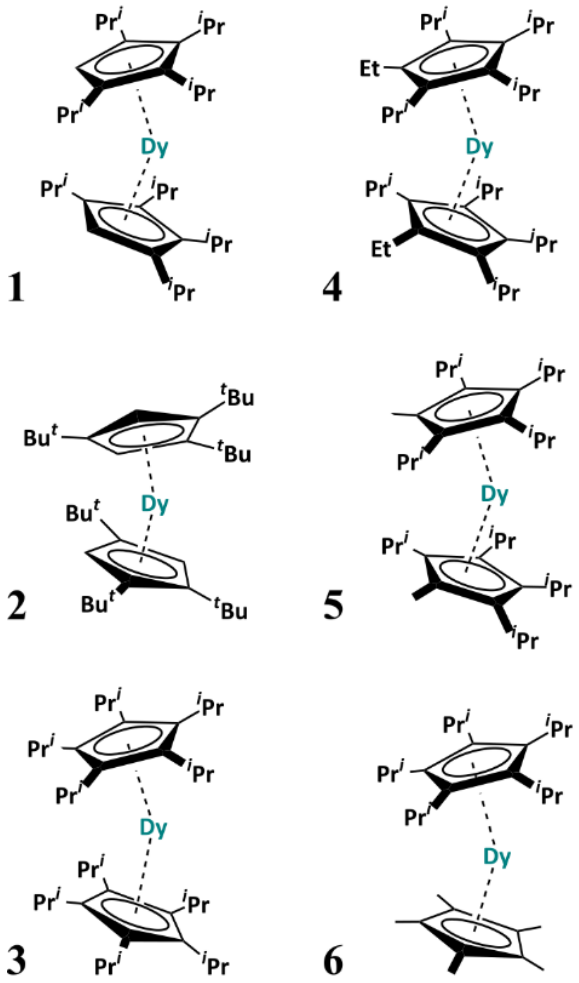

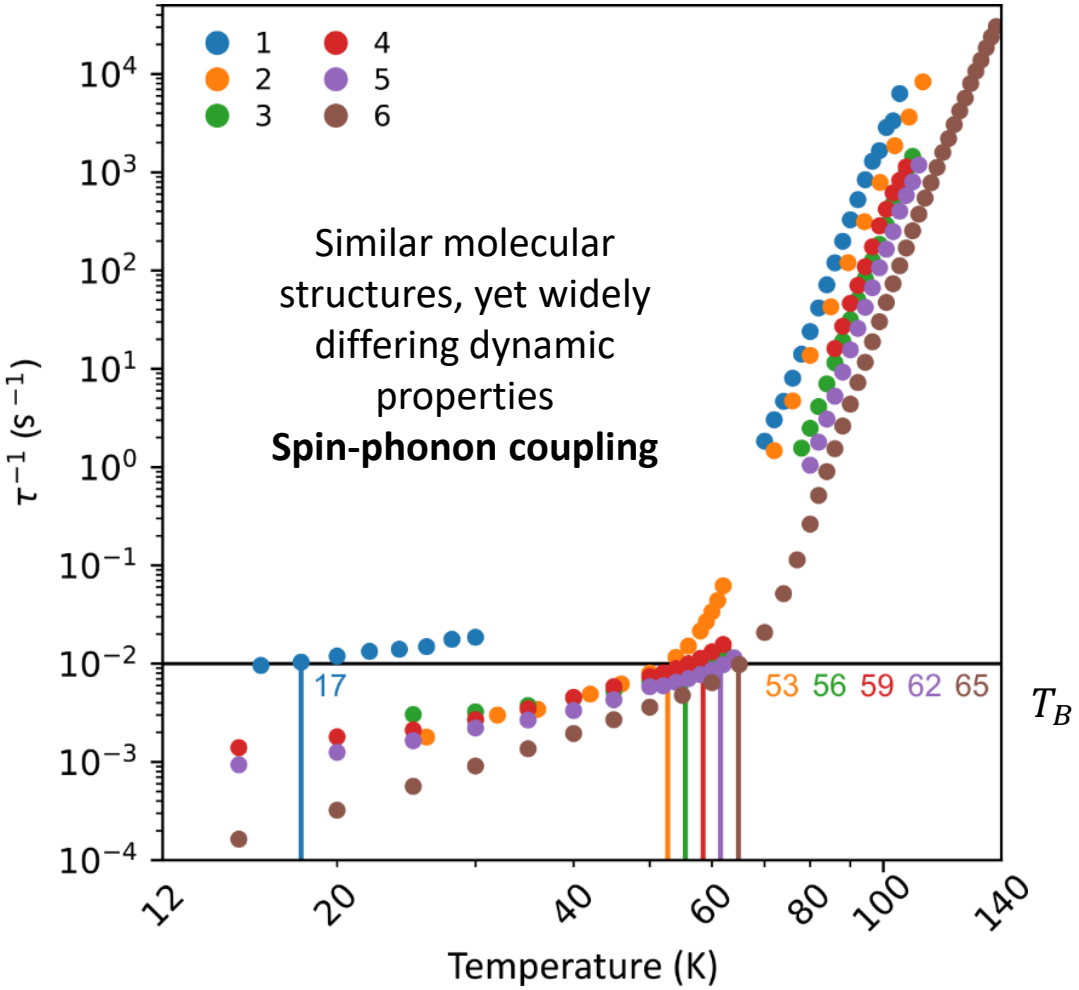

Single Molecule Magnets

- *Our approach to ab initio spin dynamics*

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  Geometry optimisation & **frequency** calculation of gas-phase molecule (DFT-PBE)

  Vibronic coupling – distort along normal modes, calculate electronic structure (CASSCF) and refer to equilibrium one (CFPs)

  - Taylor series for CFPs' dependence on distortion to describe *spin-phonon coupling* Hamiltonian

$$\hat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^{k} {B_k}^q \theta_k {\hat{O}_k}^q$$

$${B_k}^q(Q_j, Q_j', \cdots) = {B_k}^q(Q_{eq}) + \sum_{j}^{3N-6} Q_j \left(\frac{\partial {B_k}^q}{\partial Q_j}\right)_{eq}$$

$$\hat{H}_{SP,j} = \sum_{k=2,4,6} \sum_{q=-k}^{k} {B_k}^q(Q_j) \theta_k {\hat{O}_k}^q = \sum_{k=2,4,6} \sum_{q=-k}^{k} Q_j \left(\frac{\partial {B_k}^q}{\partial Q_j}\right)_{eq} \theta_k {\hat{O}_k}^q$$

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  Calculate **transition rates** γ_{if} for the Orbach process

$$\gamma_{if} = \frac{2\pi}{\hbar}\sum_j \left| \left\langle f \left| \sum_{k=2,4,6} \sum_{q=-k}^{k} \left(\frac{\partial {B_k}^q}{\partial Q_j} \right)_{eq} \theta_k {\hat{O}_k}^q \right| i \right\rangle \right|^2 \left| \langle n_j \pm 1 | Q | n_j \rangle \right|^2 \rho_j(\Delta E_{fi})$$

$\langle f \left| \hat{H}^e_{SP,j} \right| i \rangle$ → Does the vibrational motion affect Dy?

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  $\langle n_j \pm 1|Q|n_j\rangle$ → Is the vibrational mode occupied at transition energy?

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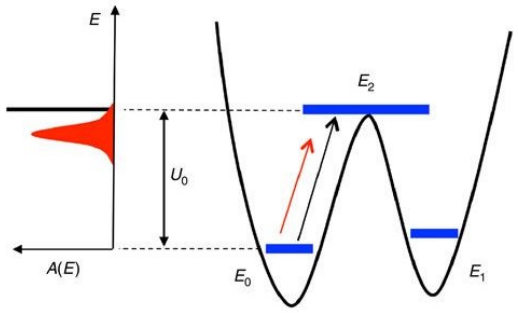

Nat. comm. **2017**, *8*, 14620

$\rho_j(\Delta E_{fi})$ → How close in energy are the vibration to the electronic state?
(only free parameter in our approach)

Single Molecule Magnets

- *Our approach to ab initio spin dynamics*

Geometry optimisation & **frequency** calculation of gas-phase molecule (DFT-PBE)

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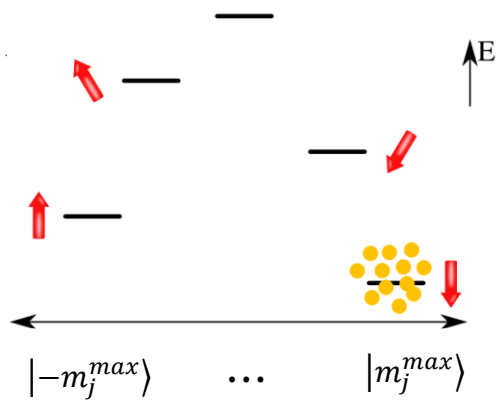
Simulate **dynamics** as a classical kinetic process master matrix

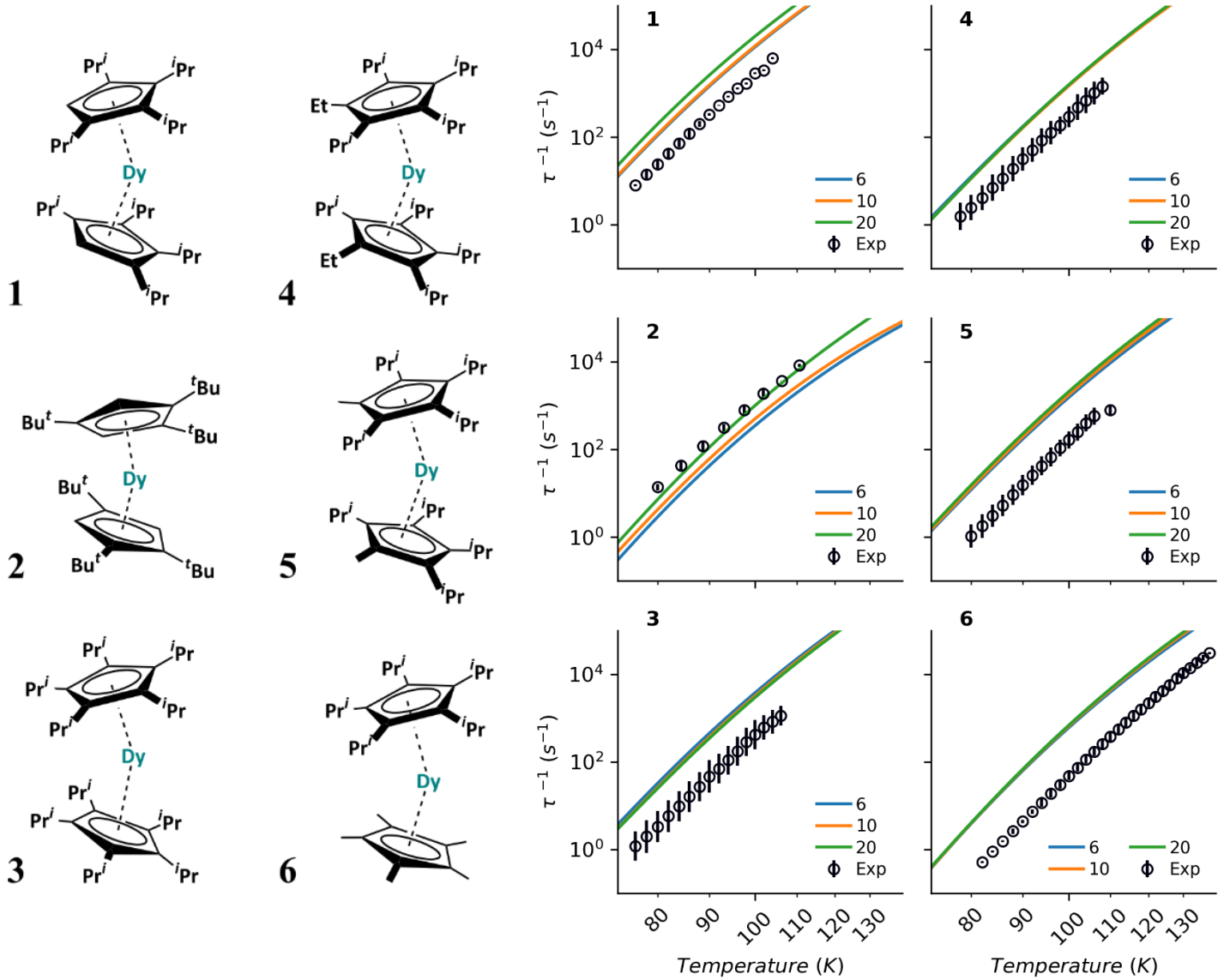
$$\frac{d}{dt}p_i(t) = \sum_{f \neq i}[\gamma_{if}p_f(t) - \gamma_{fi}p_i(t)]$$



Diagonalise matrix $\mathbf{\Gamma}$ at different T and obtain τ to compare directly to relaxation profiles.

Single Molecule Magnets

- *Our approach to ab initio spin dynamics* – comparison to experiment (*JACS.* **2021**, *143*, 15, 5943)

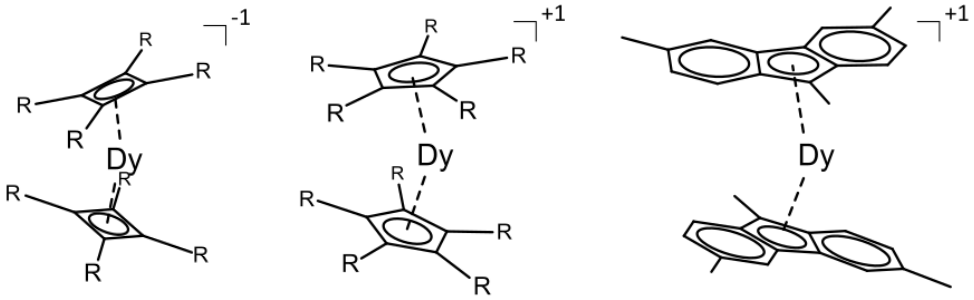


- FWHM independent.
- Consistent overestimation of τ by a factor of *ca.* 10.
- Correct ordering of the calculated τ.
- Our method can be confidently employed as a predictive tool.

Comparison of experimental (circles) and *ab initio* calculated (lines) relaxation rates for **1**–**6**. Fixed fwhm line widths of 6 (blue), 10 (orange), and 20 cm^{-1} (green) are employed.

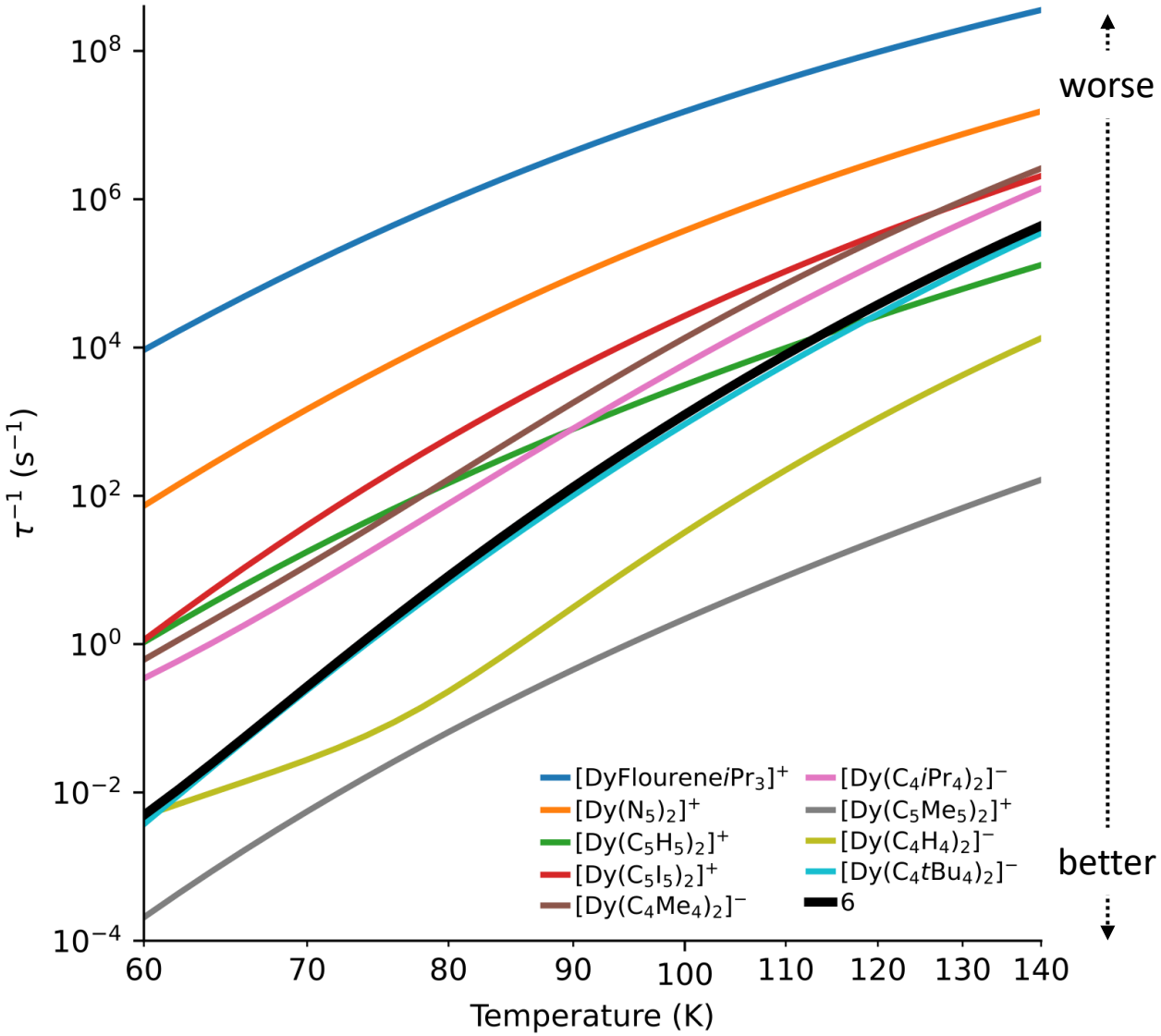
Single Molecule Magnets

- *Our approach to ab initio spin dynamics* – can we do **better**? (*JACS.* **2021**, *143*, 15, 5943)

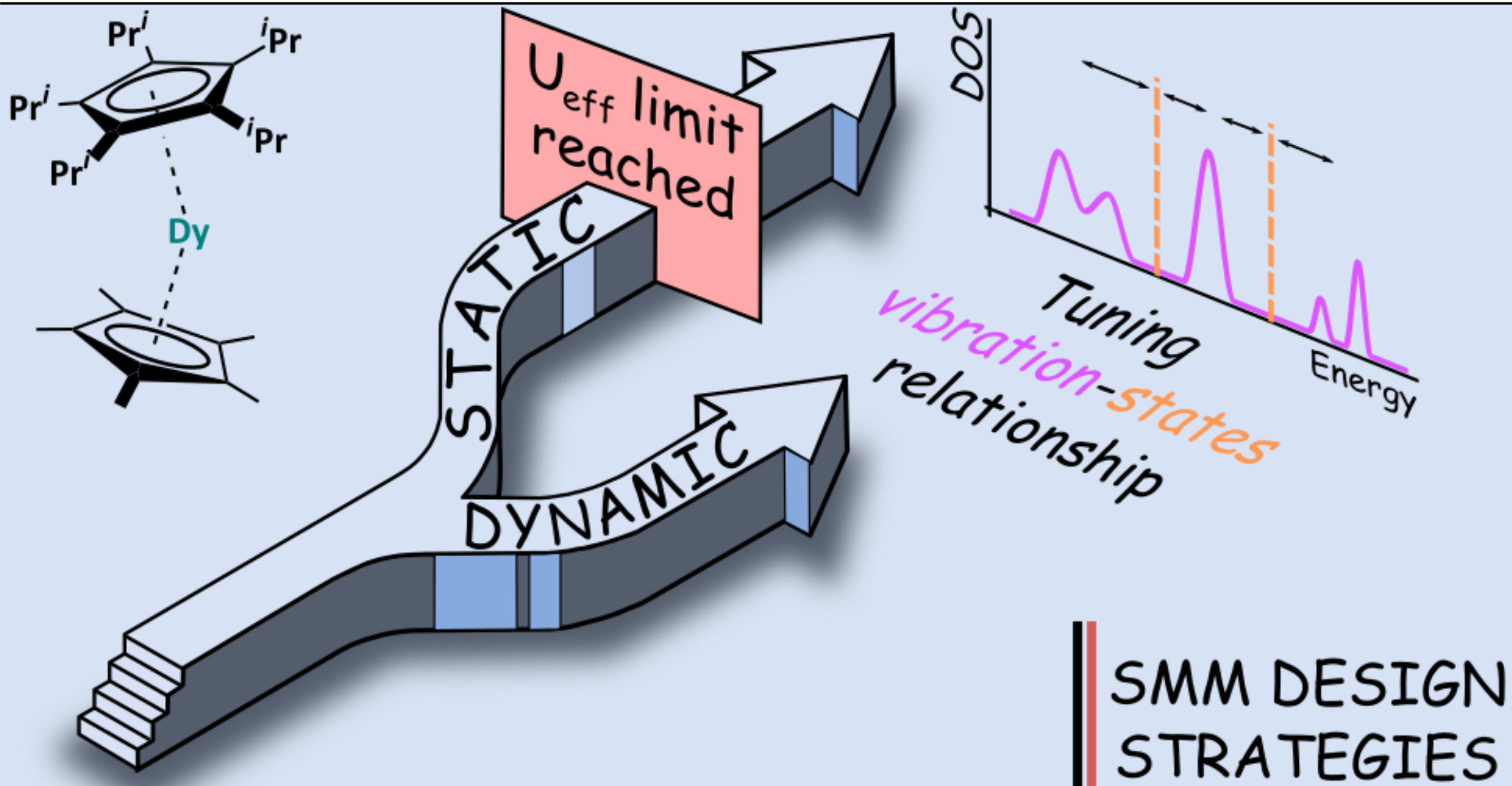


Proposed compounds aim at maximising U^{eff} by tweaking:

- Distances to ligands.
- Angle between ligands and Dy.
- Charge of ligands.



Single Molecule Magnets



Outline

- Motivation
- Molecular Magnetism
  - Experimental characterisation
  - Theory and computation
- Single Molecule Magnets
  - What makes an SMMs and why do we focus on Dy(III)?
  - Molecular design: from static to dynamic properties
- Organic Radicals
  - How to trick metal-free molecules into not forming bonds: topology
  - Impact of structural flexibility
- What's next?

Organic Radicals

- *How to trick metal-free molecules into not forming bonds: topological stabilisation of open-shell states*

  Multiple ways to generate **monoradicals**: captodative, photolysis, redox – *not* discussed here

  Di/polyradicals through extended π-systems and topological criteria: polycyclic aromatic hydrocarbons (PAHs)

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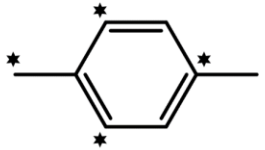
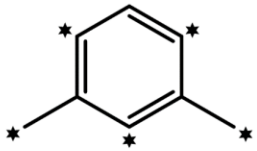
  - Lattice classification → odd alternant with non-disjoint non-bonding MOs are target





$$N = n^{starred} - n^{non-starred}$$

$$N^{even} = 0 \,/\, N^{odd} = 2$$

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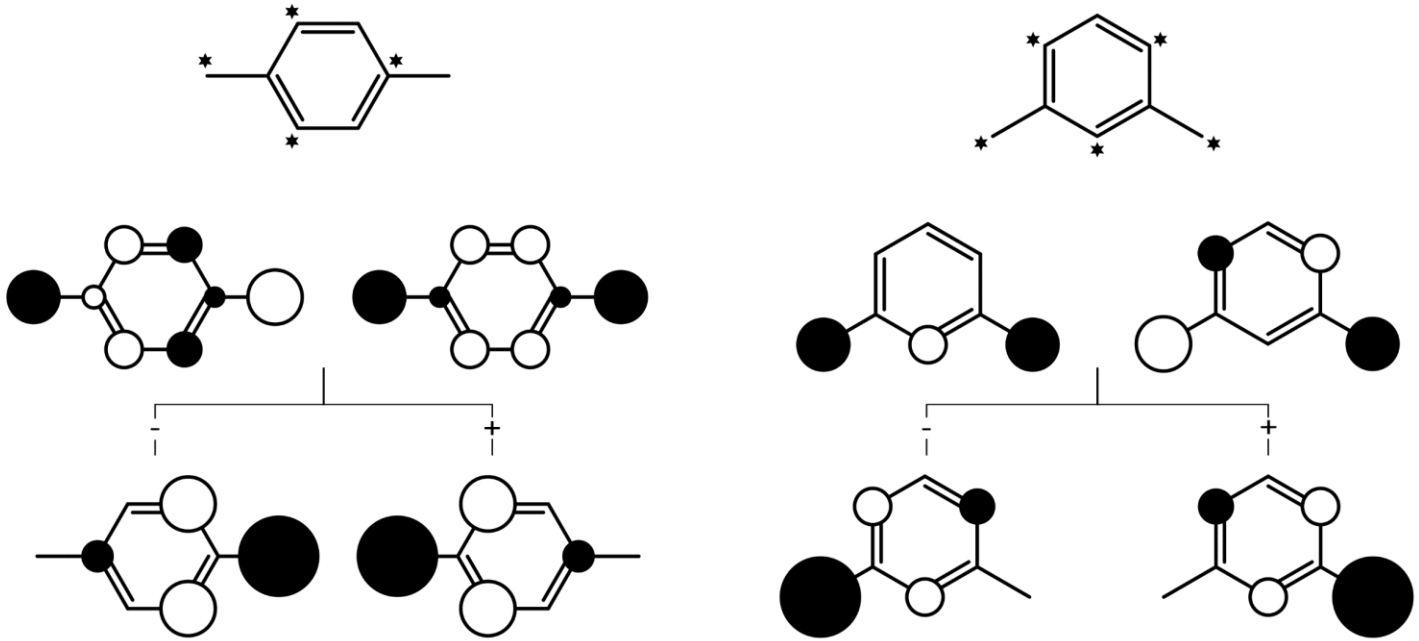

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How much do NBMOs overlap?

A little for even / A lot for odd

(because orthogonal and degenerate, $S_{ab} \sim 0$ while $K_{ab} \neq 0$ with $\Delta E_{ST} = -2K_{ab}$)

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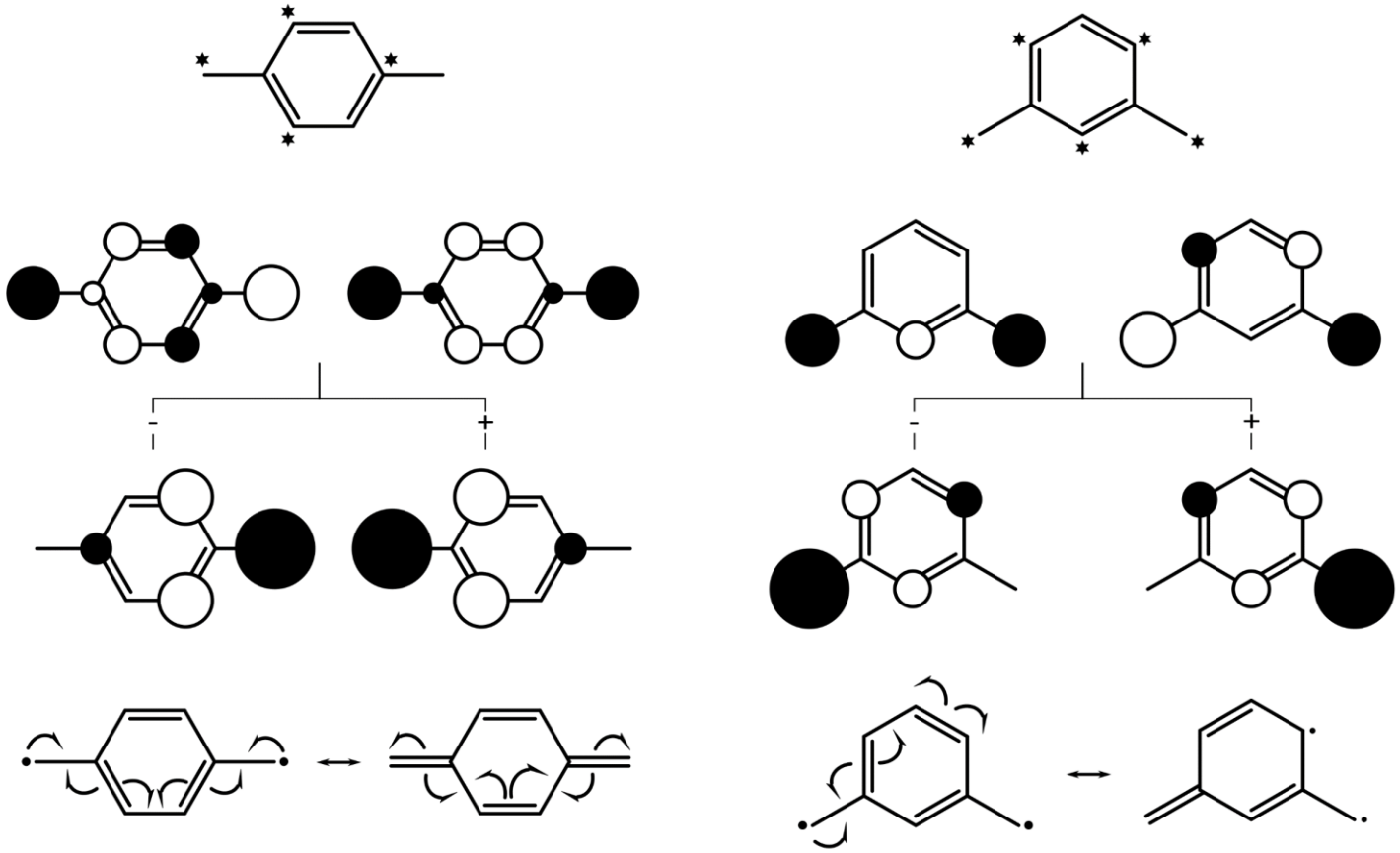

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Broken bonds to access diamagnetic state?

0 for even / 1 for odd

Organic Radicals

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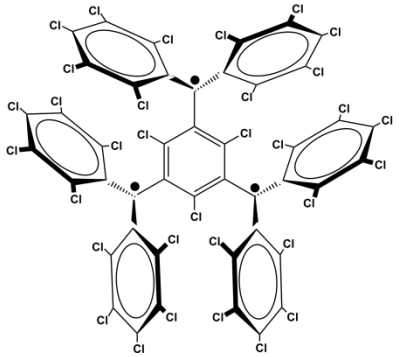
  Caution: these are approximate guidelines derived for idealised systems. Real molecules are MUCH trickier

  - Other crucial factors for radical stabilisation: kinetic (steric) and thermodynamic (delocalisation)
  - Radicals are particularly sensitive to solvent effects
  - Nevertheless useful

Organic Radicals

- *Impact of structural flexibility – A molecular junction* (*Nano Lett.* **2016***, 16,* 3, 2066–2071)

  Experimental inconsistencies (IETS)



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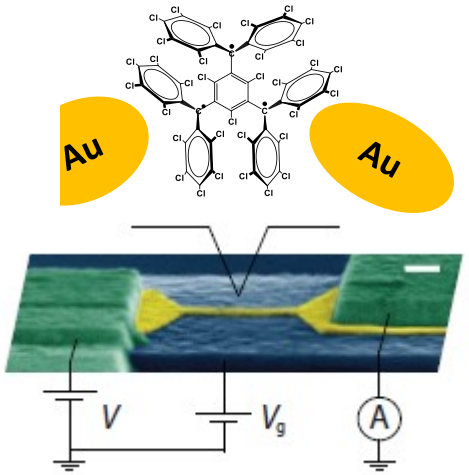
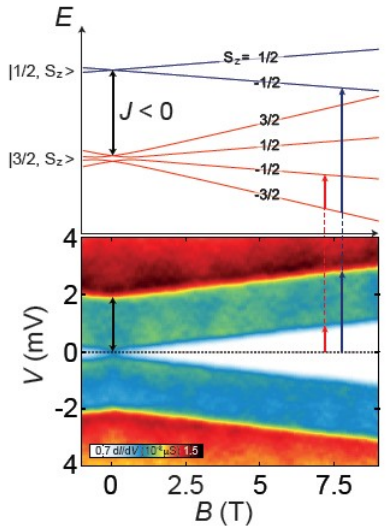
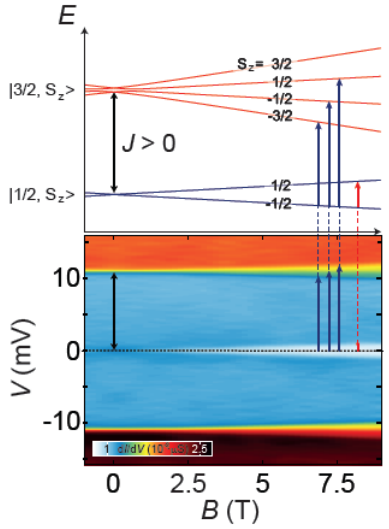
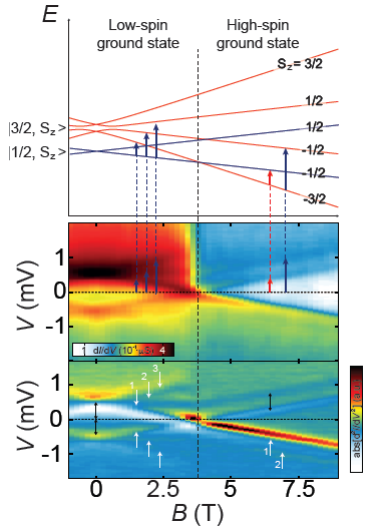




Sample #1



Sample #2



Sample #3

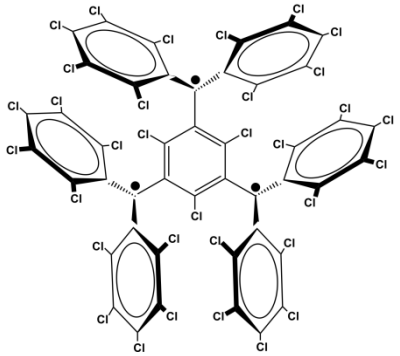
Ground state changes with sample

Organic Radicals

- *Impact of structural flexibility – A molecular junction* (*Nano Lett.* **2016**, *16,* 3, 2066–2071)

  Computational insight

  - Ising Hamiltonian to calculate exchange interaction as $\widehat{H} = \sum_{\langle i,j \rangle} J_{ij}\, \hat{S}_i^z \hat{S}_j^z$ with $J_{12} = J_{23} = J_{13} = J$ (isosceles)
  - Broken symmetry (DFT) approach: $HS = |\alpha\alpha\alpha\rangle$, $LS = |\alpha\alpha\beta\rangle = |\alpha\beta\alpha\rangle = |\beta\alpha\alpha\rangle \rightarrow E_{|LS\rangle} - E_{|HS\rangle} = J$



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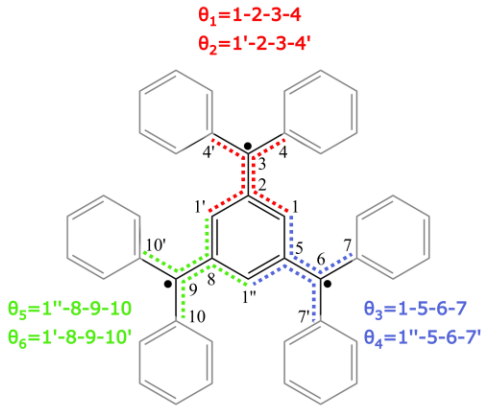
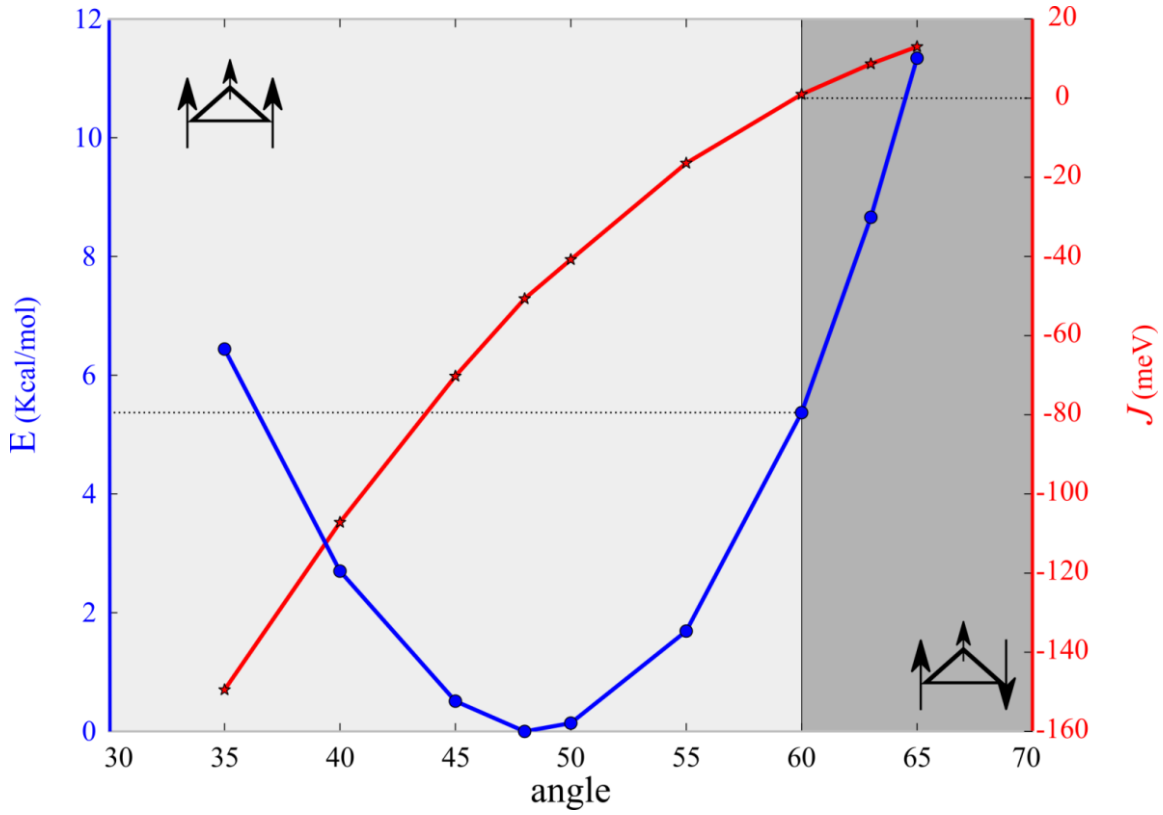
  - Explore torsion with dihedrals





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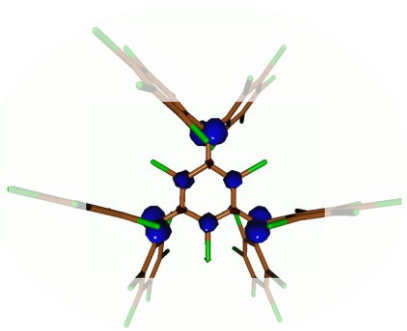
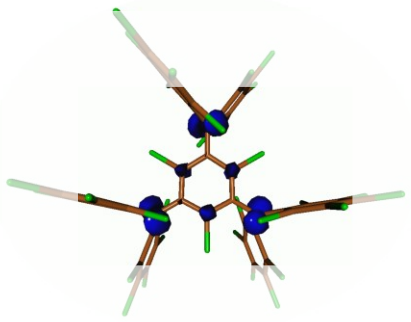
  - Explore torsion with dihedrals
  - J inversion by π-disruption (non-disjoint → disjoint)

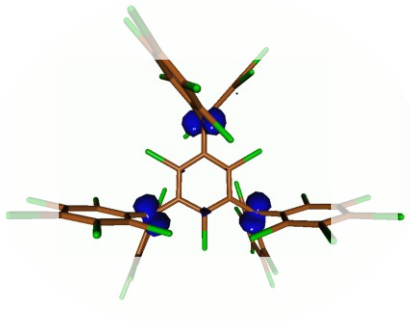
Spin densities @



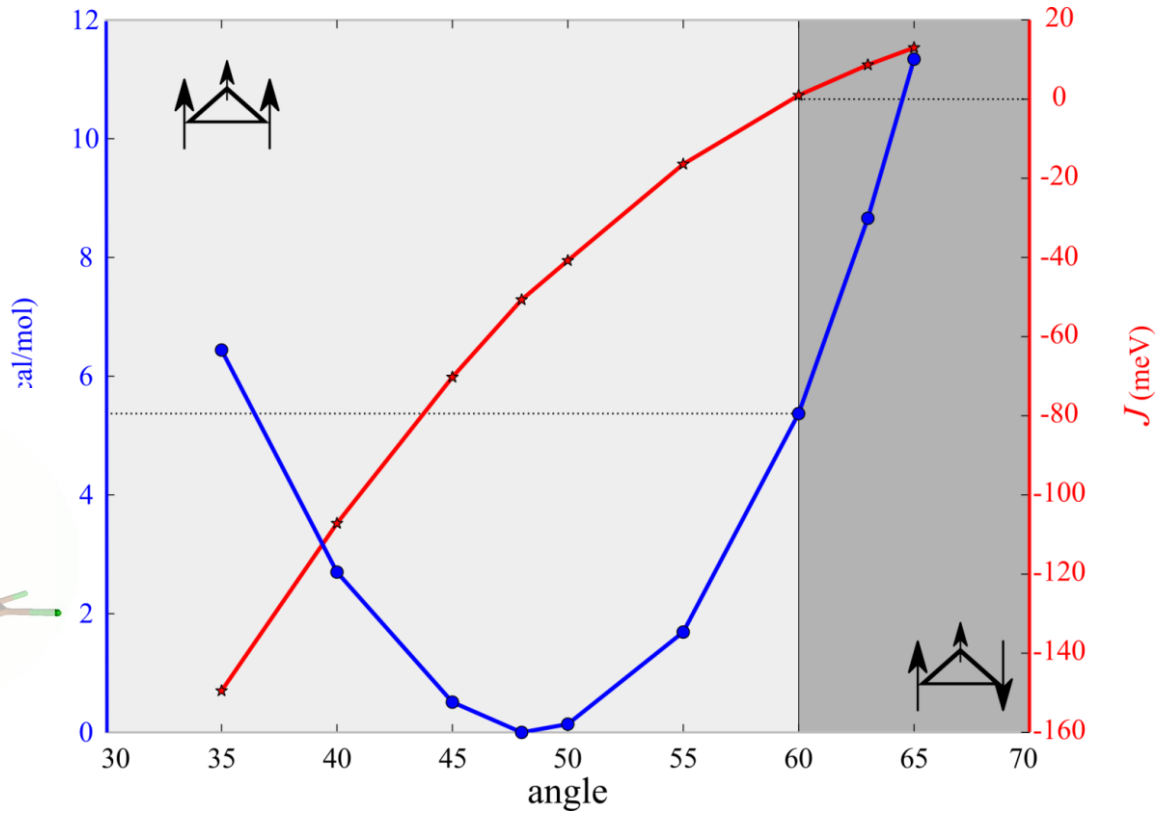
35 °



equilibrium



65 °



Organic Radicals

- *Impact of structural flexibility – Chirality meets ferromagnetism* (*JACS*, **2016**, *138* (16), 5271)

Organic Radicals

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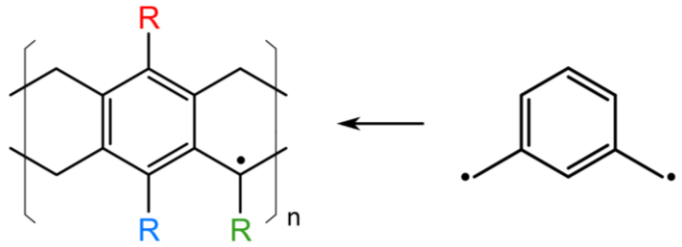
  Building blocks towards low-dimensionality systems

  - Previous failed synthetic efforts imposed planarity



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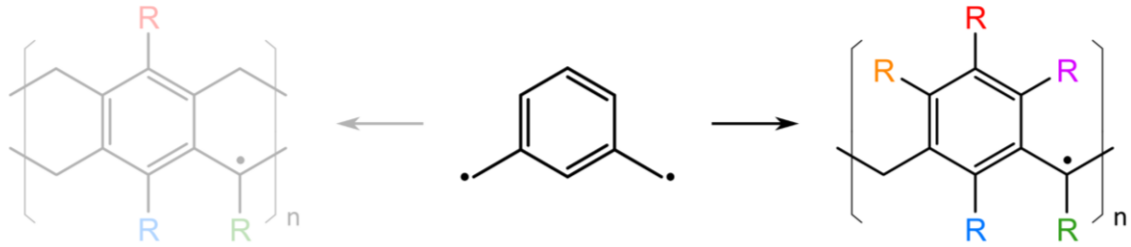

  - B3LYP calculations in periodic & gas-phase to compare structural and magnetic properties of different conformers
  - Broken symmetry approach to *1st neighbours interactions*

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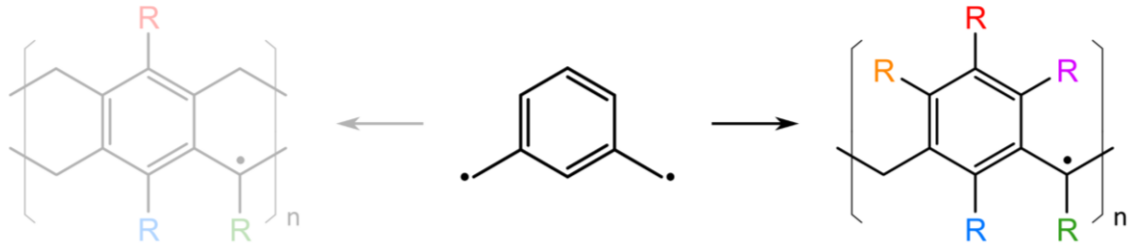
Building blocks towards low-dimensionality systems



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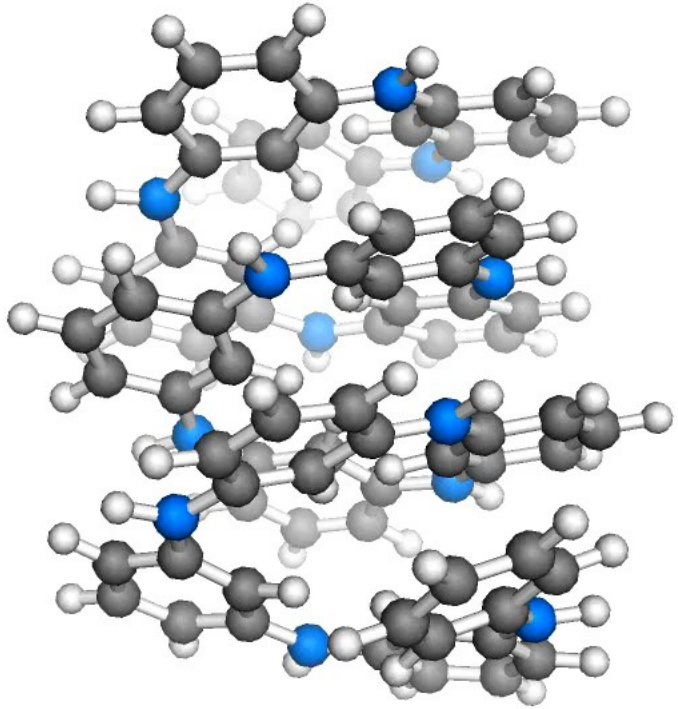
Can the inherent structural flexibility be exploited?

- B3LYP calculations in periodic & gas-phase to compare structural and magnetic properties of different conformers
- Broken symmetry approach to *1st neighbours interactions*
- Linear *vs* helix:

  Helix structure is **stabilised** 2.8 Kcal/mol per radical center

  J is 18% **larger** in helix (~ 390 cm^{-1})

- Ferromagnetism & chirality on the same molecular platform

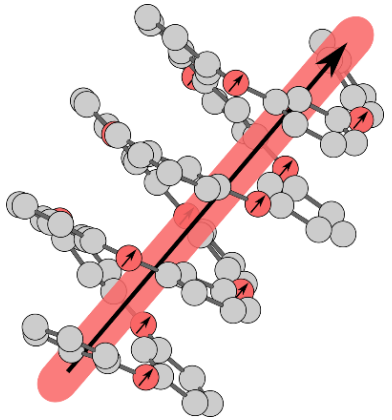


Organic Radicals

- *Impact of structural flexibility – Chirality meets ferromagnetism*

Let's speculate

- Synthetically feasible
- Structural anisotropy induces magnetic anisotropy
- Enantiomeric separation
- Functional



Organic Radicals

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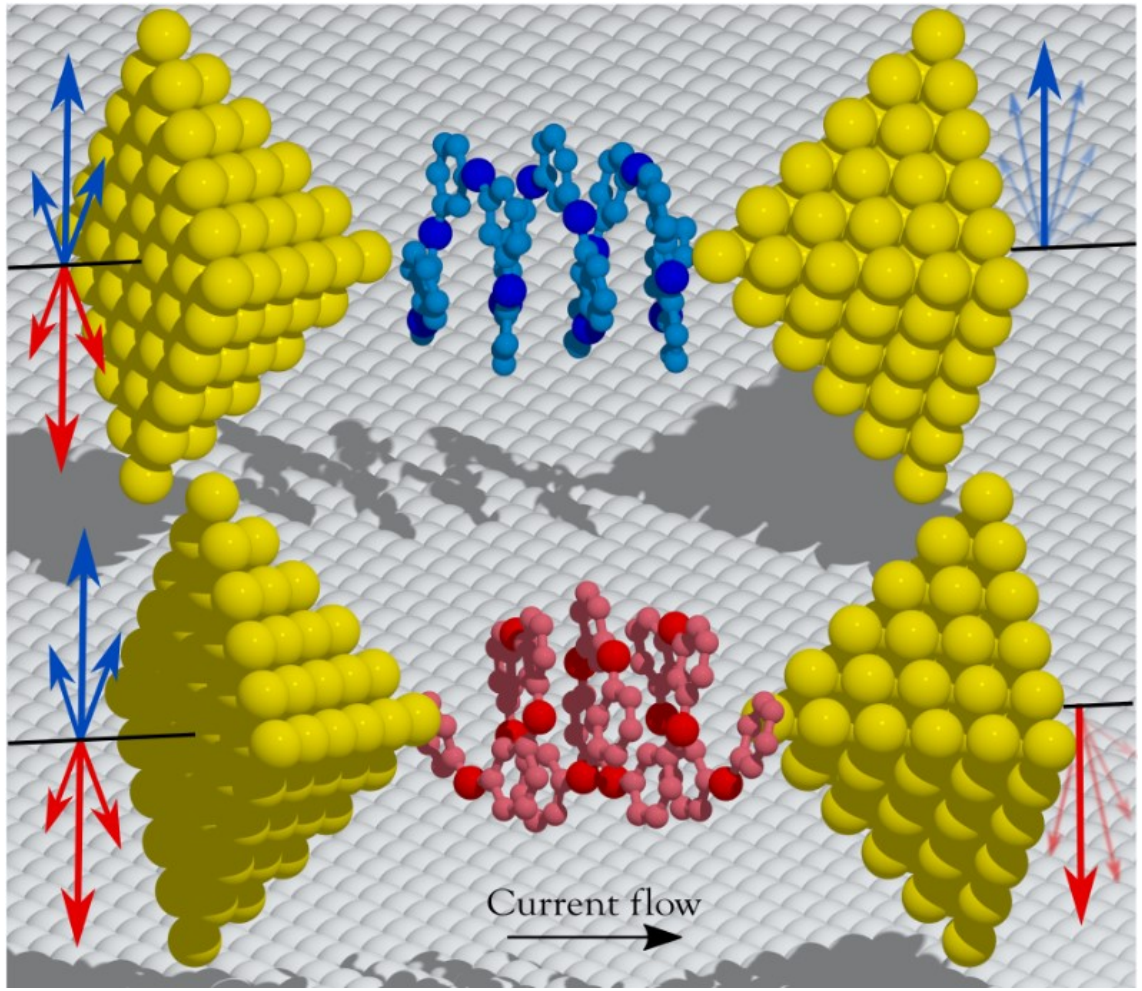
Proposal as **spin-filter**

- Transport calculations (?)



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