El Escorial, May 11th 2023

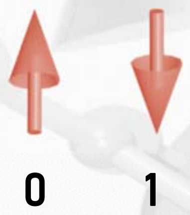
ESMolNa
European School on Molecular Nanoscience

Heterometallic Lanthanide Complexes as Molecular Quantum Processors

GUILLEM AROMI

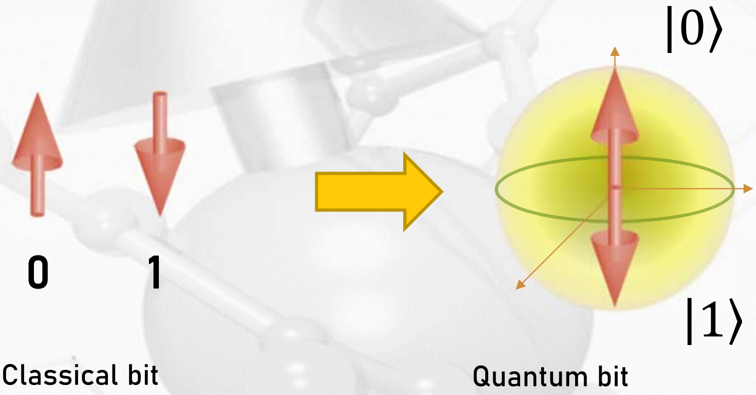
UNIVERSITAT DE BARCELONA

The Qubits of Quantum Computing (QC)

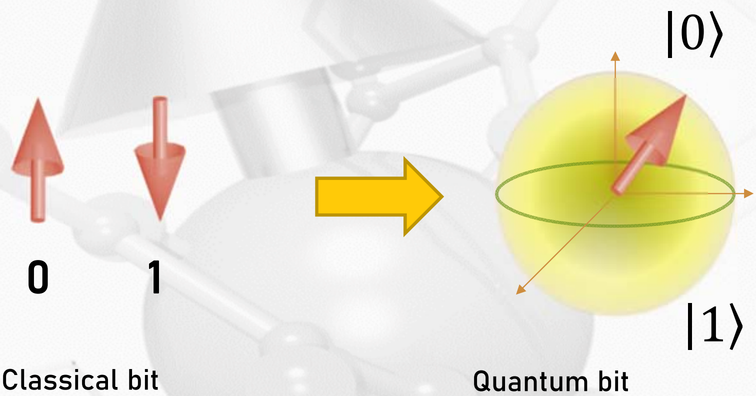


Classical bit

The Qubits of Quantum Computing (QC)



The Qubits of Quantum Computing (QC)



$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

Quantum superpositions allow "Quantum Parallellism"

Qubits Requirements

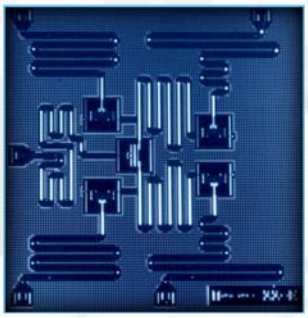
TWO QUANTUM LEVELS

SCALABILITY

LONG COHERENCE TIME

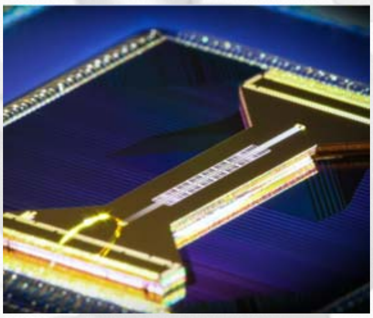
Qubits Realizations

Superconducting Circuits



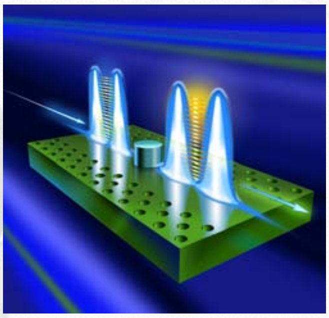
Science ***2013***, *339*, 1169

Trapped Ions



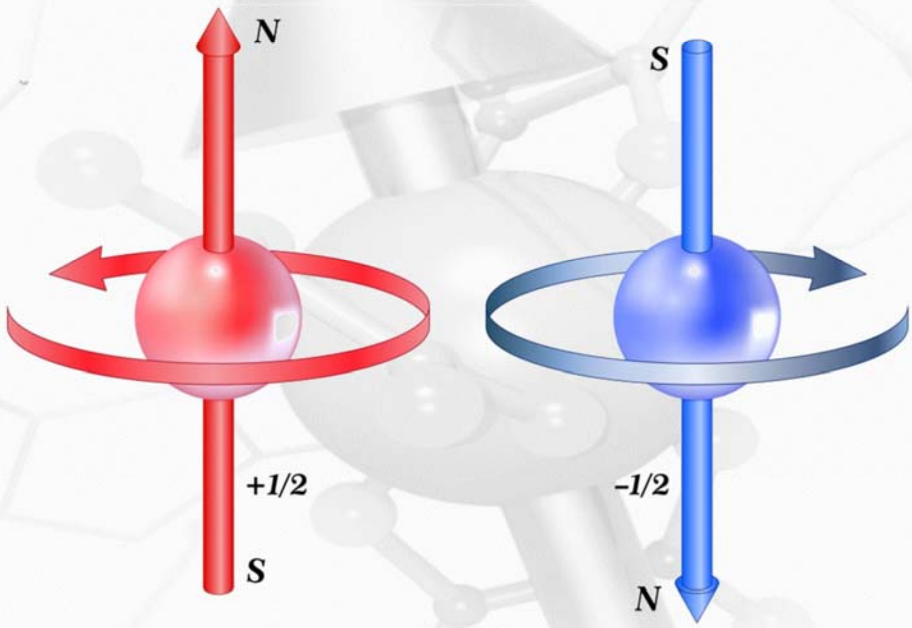
Nature 2020, *587*, 342

Photons

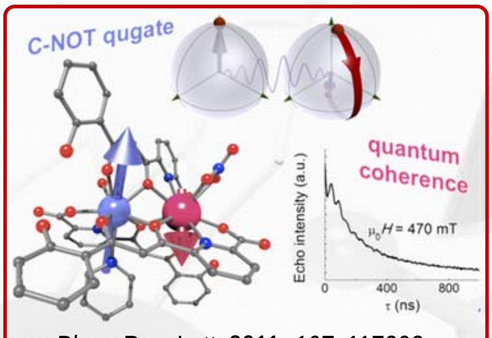


Science ***2021***, *373*, 1436

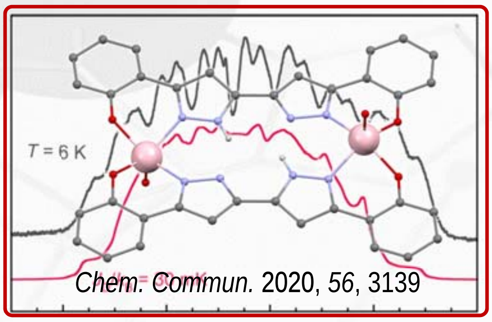
Electron Spin Qubits



Molecular Design of Spin-based Quantum Gates

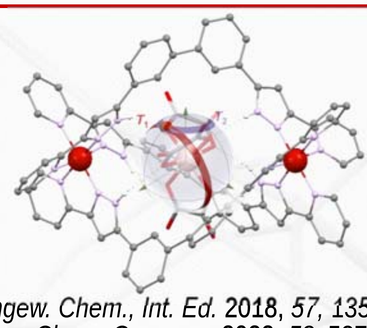


Phys. Rev. Lett. 2011, *107*, 117203
J. Am. Chem. Soc. 2014, *136*, 14215
Commun. Chem. 2020, *3*, 176

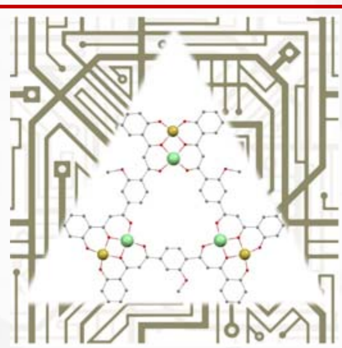


Chem. Commun. 2020, *56*, 3139

Chem., Eur. J. 2017, *23*, 13648



Angew. Chem., Int. Ed. 2018, *57*, 13509
Chem. Commun. 2022, *58*, 5375

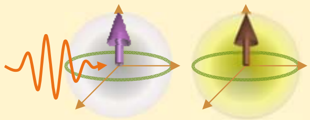


Chem. Commun. 2022, *58*, 7530

2Qubit Quantum Gates

CNOT Gate

CONTROL TARGET

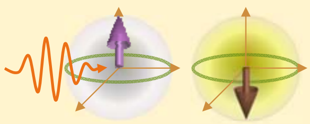


$$|11\rangle \leftrightarrow |10\rangle$$
$$|10\rangle \leftrightarrow |11\rangle$$
$$|01\rangle \longrightarrow |01\rangle$$
$$|00\rangle \longrightarrow |00\rangle$$

2Qubit Quantum Gates

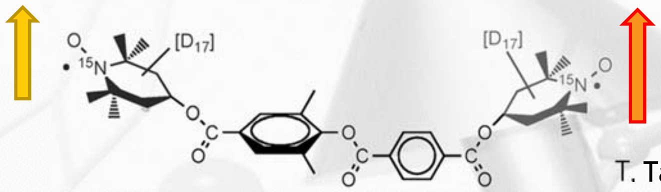
CNOT Gate

CONTROL TARGET

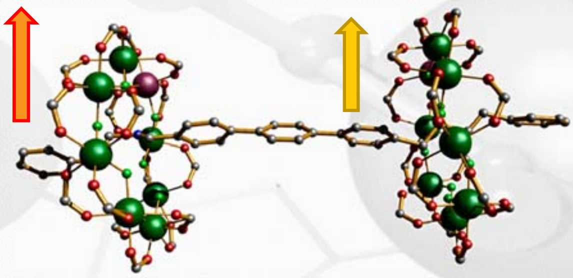


$$|11\rangle \leftrightarrow |10\rangle$$
$$|10\rangle \leftrightarrow |11\rangle$$
$$|01\rangle \longrightarrow |01\rangle$$
$$|00\rangle \longrightarrow |00\rangle$$

Spin-based 2Qubit Quantum Gates



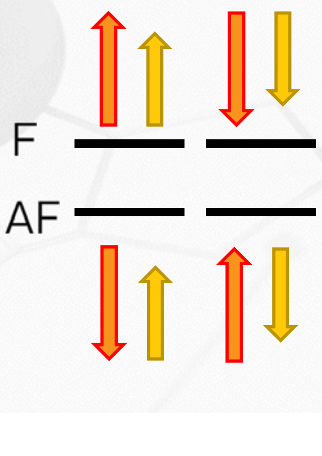
T. Takui, *et al.*
Angew. Chem., Int. Ed. **2012**, *51*, 9860-9864.



Winpenny, *et al.*
Nat. Nanotechnol. **2008**, 4, 173–178

How Could we build a CNOT with Rare Earths?

- Two Inequivalent Ln's
- Weakly Coupled
- Axially Anisotropic



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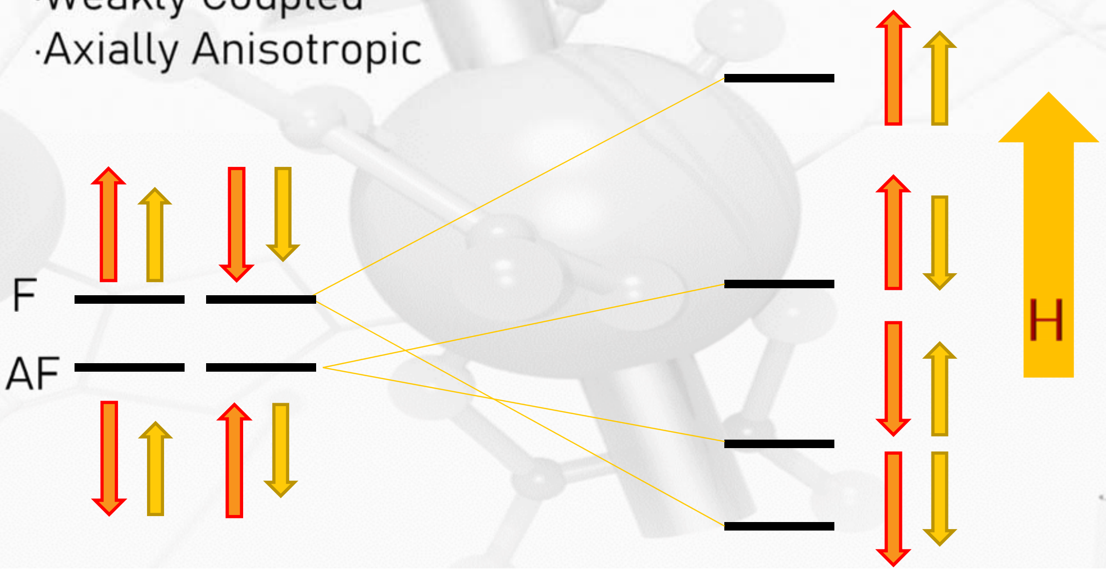

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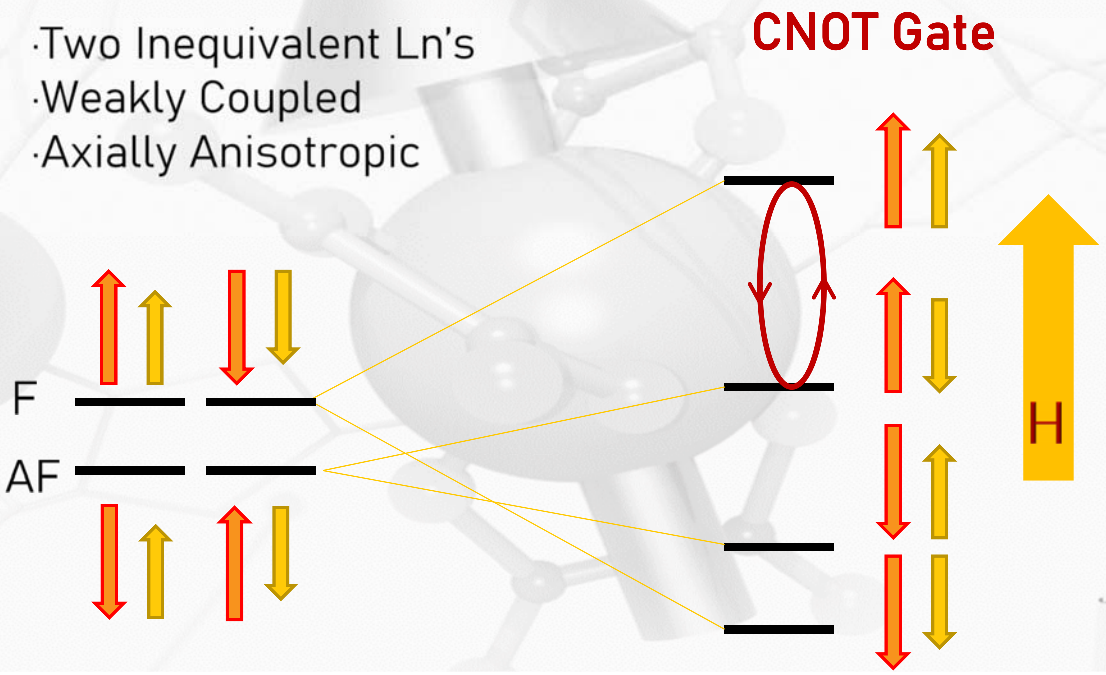
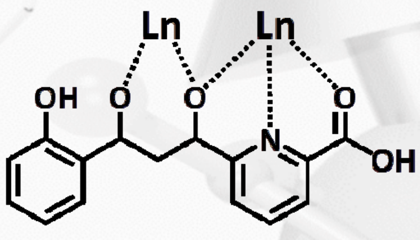
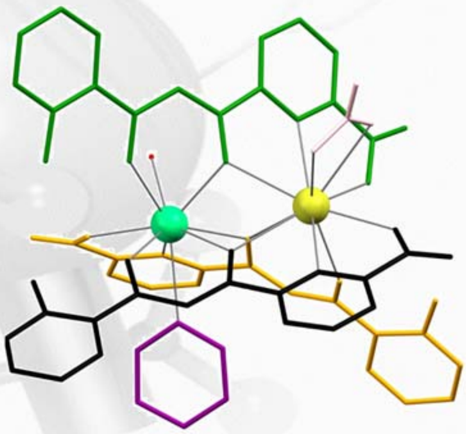


Design Strategy: Dinuclear Asymmetric Lanthanide Complexes



H_3L



Large Homometallic Series

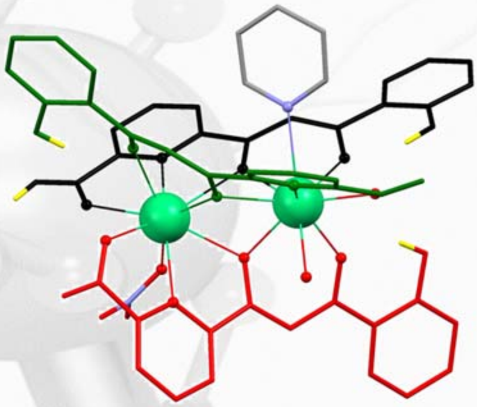
$2Ln(NO_3)_3 \cdot xH_2O + 3H_3L + 6py \longrightarrow$

$(pyH)[Ln_2(HL)_3(NO_3)(py)(H_2O)] + (2x-1)H_2O + 5(pyH)NO_3$

Inorg. Chem. ***2011***, *49*, 6784
Chem. Eur. J. 2013, *19*, 5881

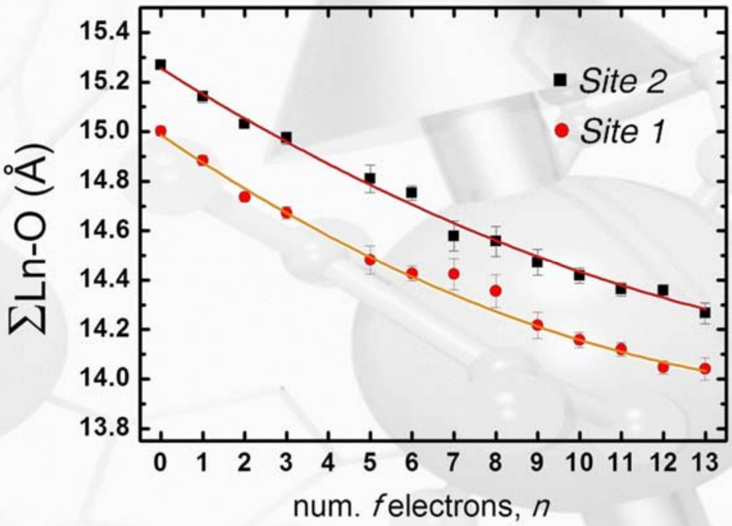
Molecular Prototypes for Spin-Based CNOT and SWAP Quantum Gates

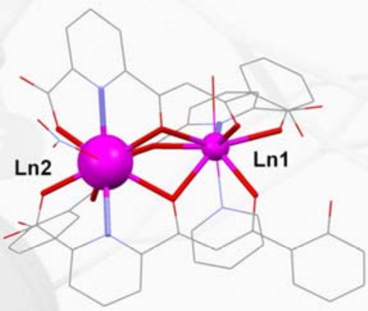
Phys. Rev. Lett. **2011**, *107*, 117203.



La Ce Pr Nd ~~Pm~~ Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Average Bond Distances to Ln

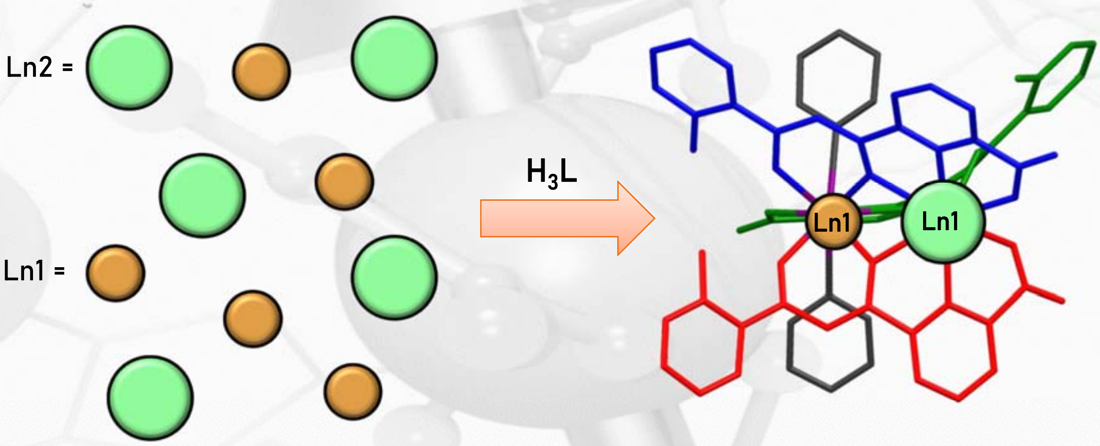




Chem., Eur. J. 2013, *19*, 5881–5891

1) Bond distances for both sites decrease throughout the series
2) Site 2 is systematically larger than site 1
3) Distance GAP between both sites is maintained

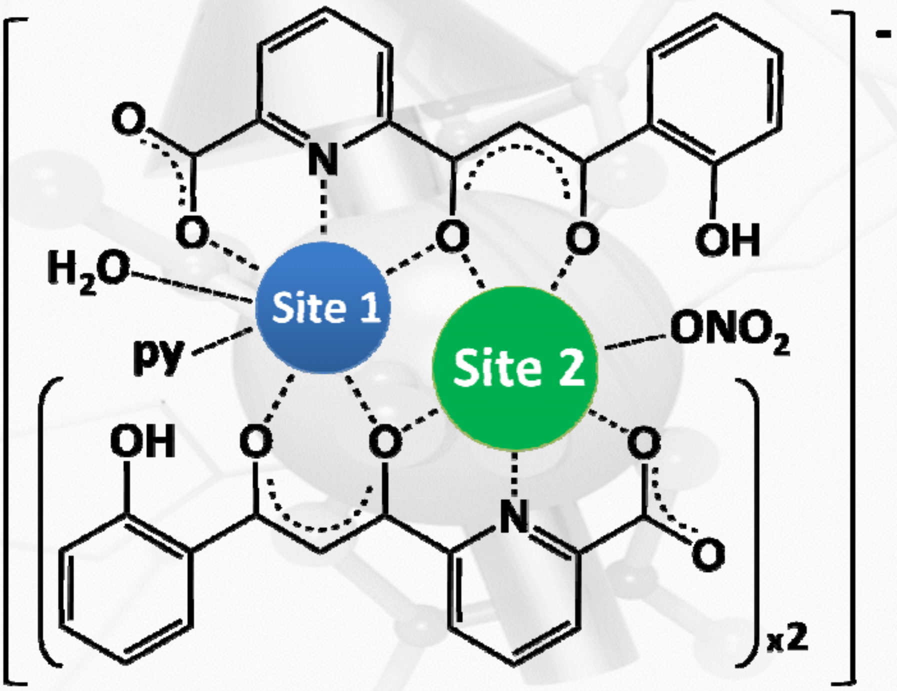
Synthesis of Heterometallic 4f-4f' Clusters



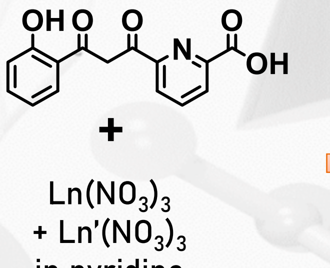
LnLn' cluster *à la carte*?

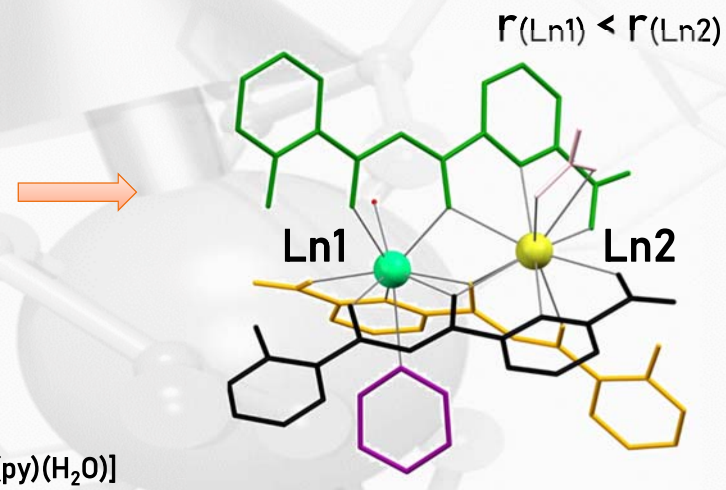
Many Possible Qugate Designs!!

Why is Site 2 larger than Site 1?



Heterometallic [LnLn'] Complexes



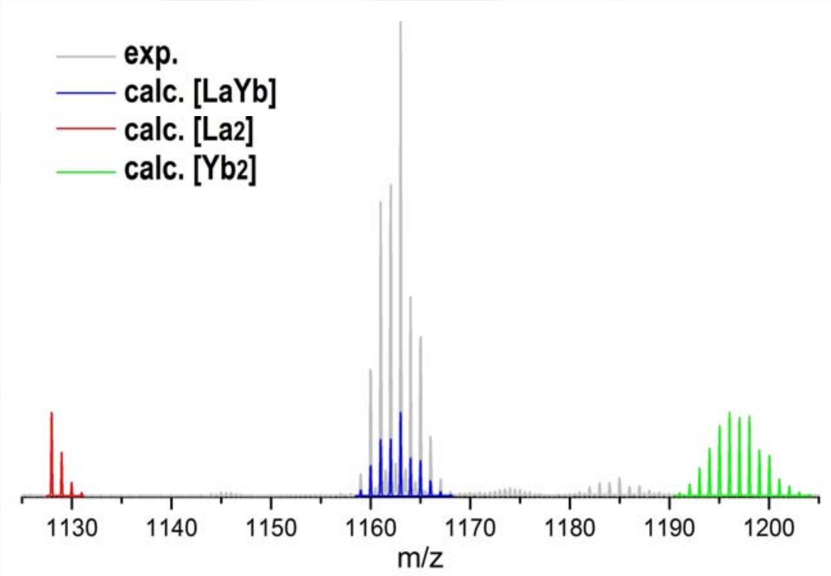


(pyH)[Ln1Ln2(HL)$_3$(NO$_3$)(py)(H$_2$O)]

J. Am. Chem. Soc. **2014**, *136*, 14215
Chem., Eur. J. **2017**, *23*, 5117
Inorg. Chem. **2018**, *57*, 8429

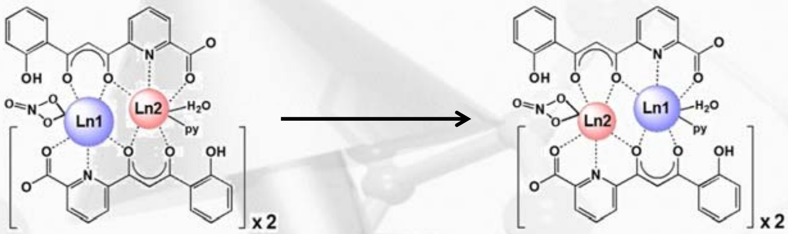
- X-Ray diffraction
- Mass Spectrometry
- Metal Analysis
- Magnetic susceptibility

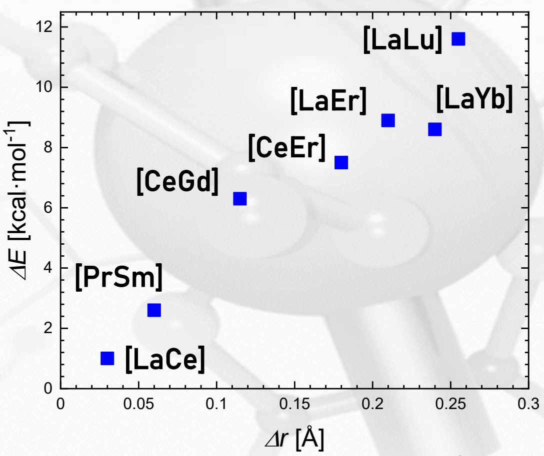
Mass Spectrometry [LnLn'] Complexes



Chem., Eur. J. **2017**, *23*, 5117

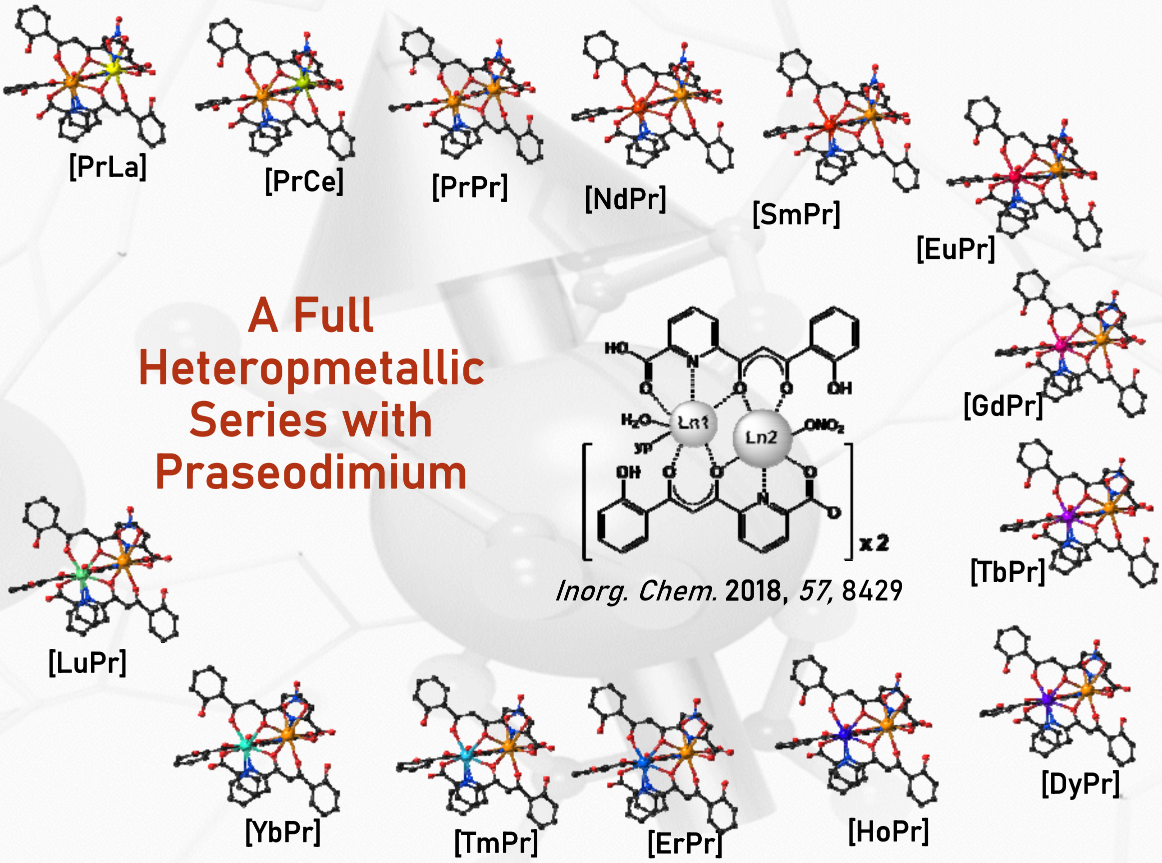
Selectivity of [LnLn'] Complexes by DFT





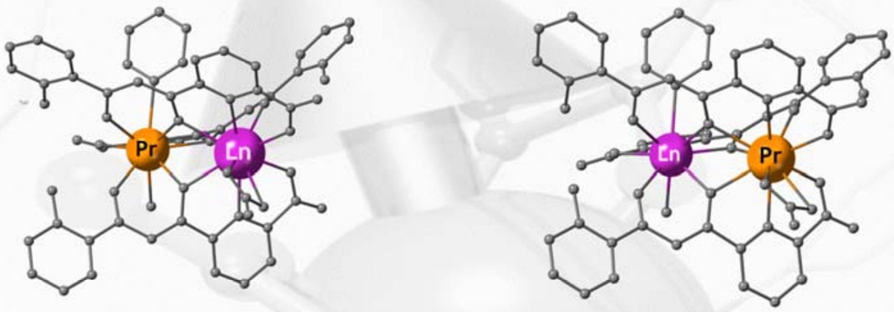
Chem., Eur. J. **2017**, *23*, 5117-5125

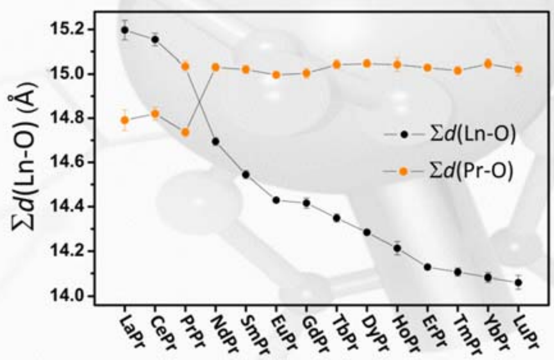
A Full Heteropmetallic Series with Praseodimium



Inorg. Chem. 2018, *57*, 8429

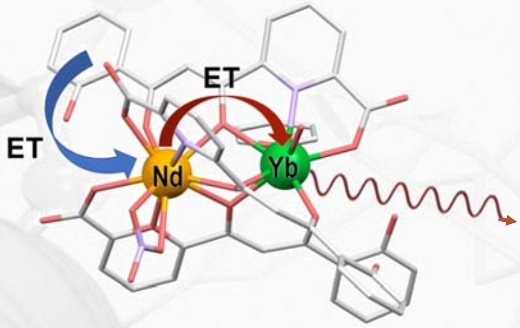
Full [PrLn] Series

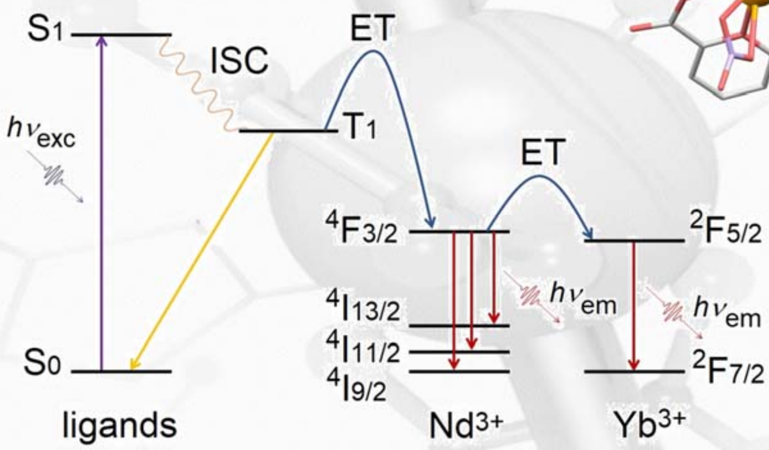




Inorg. Chem. 2018, *57*, 8429

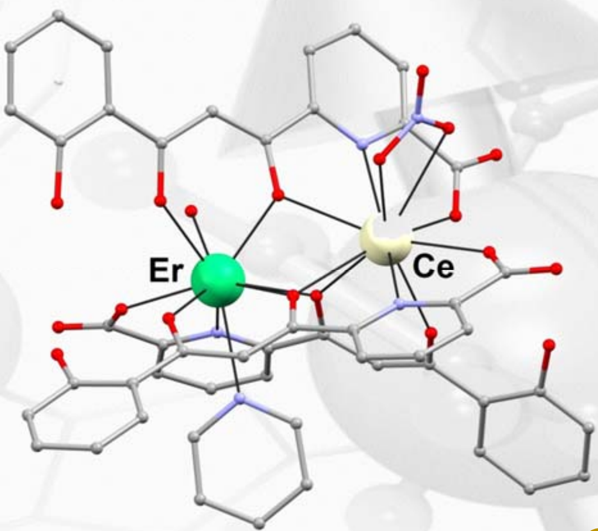
Intramolecular Heterometallic Ln-to-Ln' Energy Transfer





Chem., Eur. J. **2021**, *27*, 7288 –7299

A Spin Based Quantum Gate with [CeEr]?



$(pyH)[CeEr(H_2L)_3(NO_3)(py)_2]$

Ce(III):
J=5/2, g_J=6/7,
I = 0

NO Nuclear Spin

Er(III):
J=15/2, g_J=6/5,
I=0 (70%)

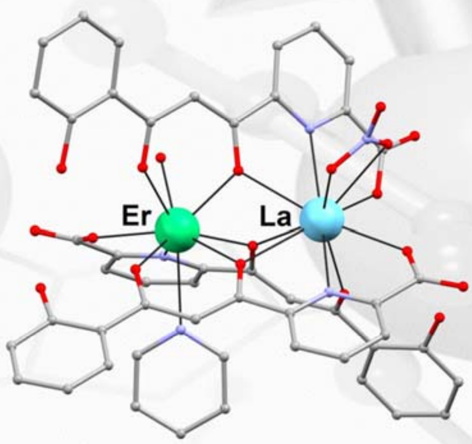
Only 23% Nuclear Spin

- Possible Long Coherence
- Both have a ground state doublet
- Very different

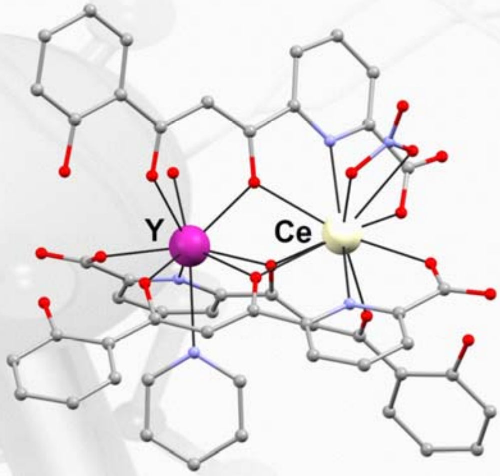
Characterization of Individual Qubits

$r_{(Er)} < r_{(La)}$

$r_{(Y)} < r_{(Ce)}$



$(pyH)[LaEr(H_2L)_3(NO_3)(py)_2]$

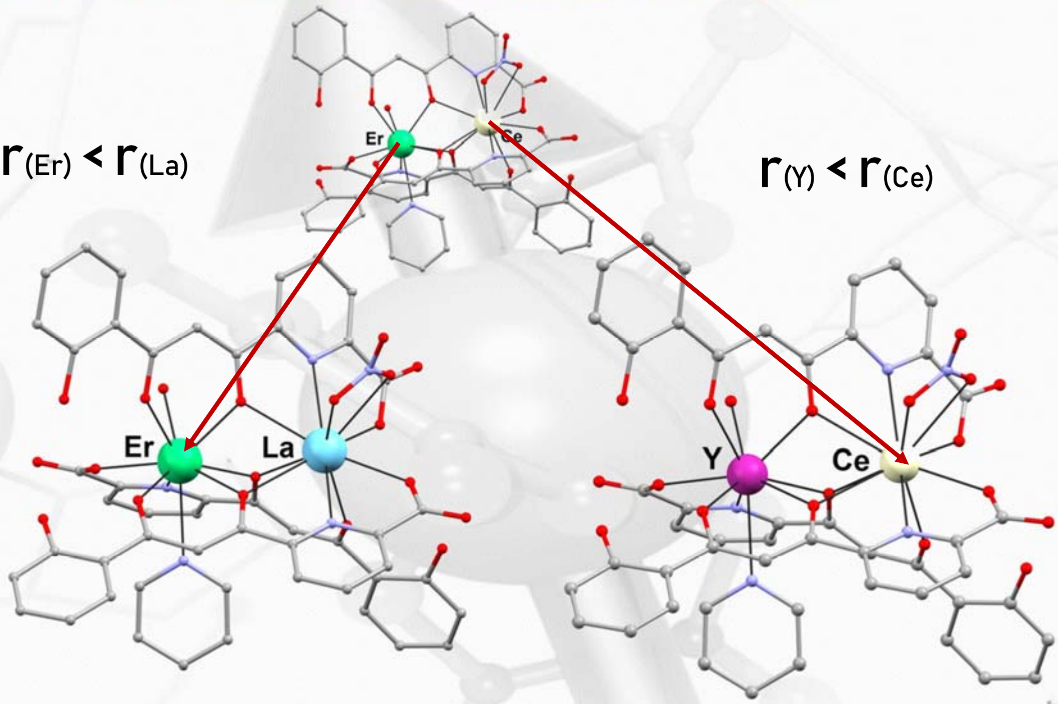


$(pyH)[CeY(H_2L)_3(NO_3)(py)_2]$

Characterization of Individual Qubits

$r_{(Er)} < r_{(La)}$

$r_{(Y)} < r_{(Ce)}$



$(pyH)[LaEr(H_2L)_3(NO_3)(py)_2]$

$(pyH)[CeY(H_2L)_3(NO_3)(py)_2]$

Characterization of Individual Qubits

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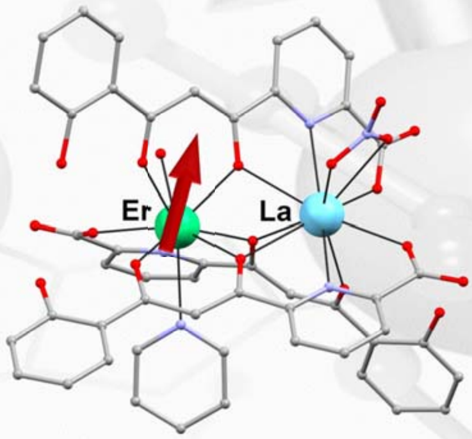

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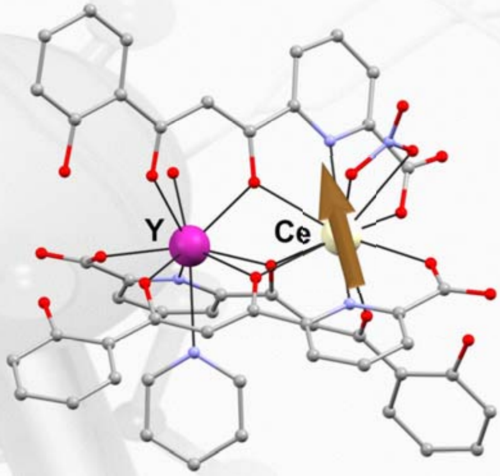
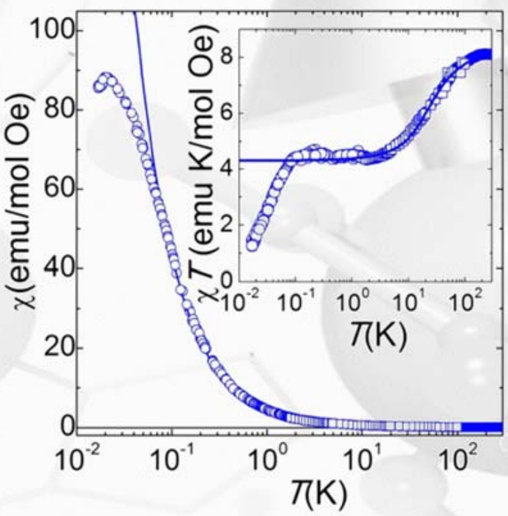
$r_{(Y)} < r_{(Ce)}$

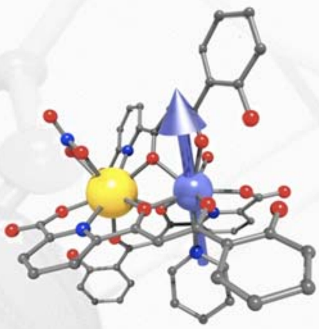


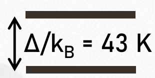
$(pyH)[CeY(H_2L)_3(NO_3)(py)_2]$

Qubits Characterization; [LaEr]

Magnetic Susceptibility





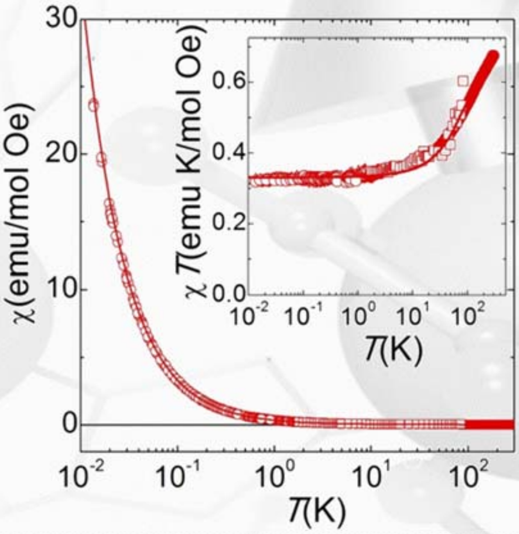


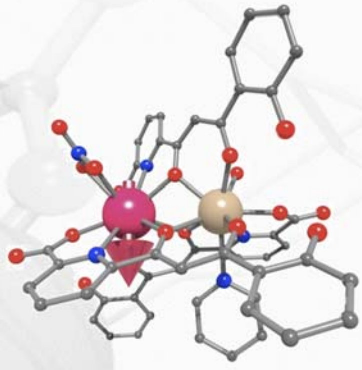
$$\chi T \approx \left(\frac{N_A \mu_B^2}{4k_B}\right)\left[C_0 + C_1\left(\frac{2k_BT}{\Delta}\right)\tanh\left(\frac{\Delta}{2k_BT}\right) + C_2\tanh\left(\frac{\Delta}{2k_BT}\right)\right]$$

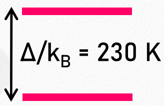
Well Isolated Ground State

Qubit Characterization; [CeY]

Magnetic Susceptibility







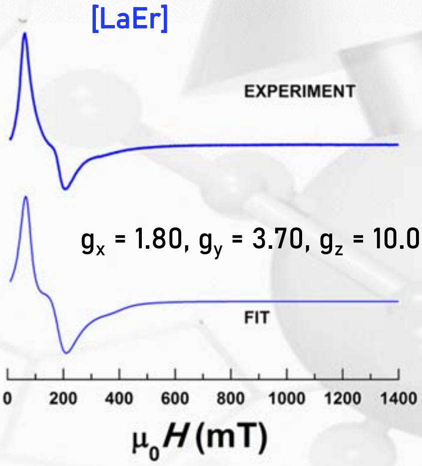
$$\chi T \approx \left(\frac{N_A \mu_B^2}{4k_B}\right)\left[C_0 + C_1\left(\frac{2k_BT}{\Delta}\right)\tanh\left(\frac{\Delta}{2k_BT}\right) + C_2\tanh\left(\frac{\Delta}{2k_BT}\right)\right]$$

Well Isolated Ground State

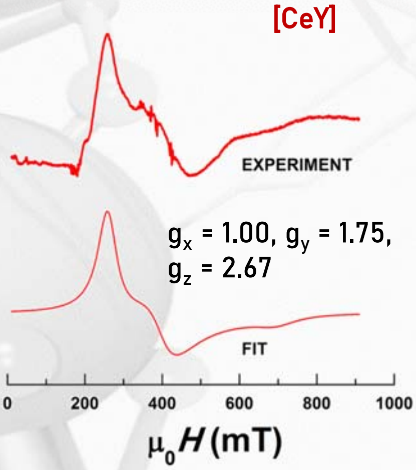
Qubit Characterization; [LaEr] *vs* [CeY]

X Band EPR; $T \leq 7$ K

[LaEr]



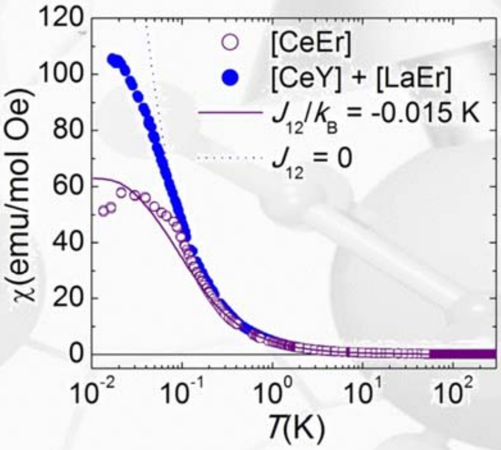
[CeY]



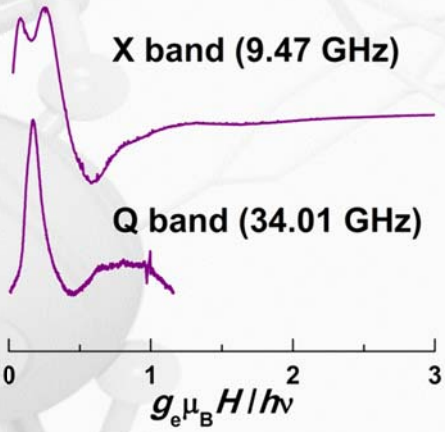
Magnetically Inequivalent

Inter-Qubit Coupling within [CeEr]

Magnetic Susceptibility



Powder EPR; $T \leq 7$ K



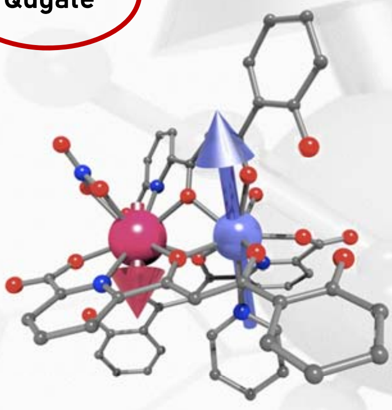
$$H = -\mu_B H \hat{g}_1 S_1 - \mu_B H \hat{g}_2 S_2 - \frac{1}{g_{J1} g_{J2}} J_{ex} S_1 \hat{g}_1 \hat{g}_2 S_2$$

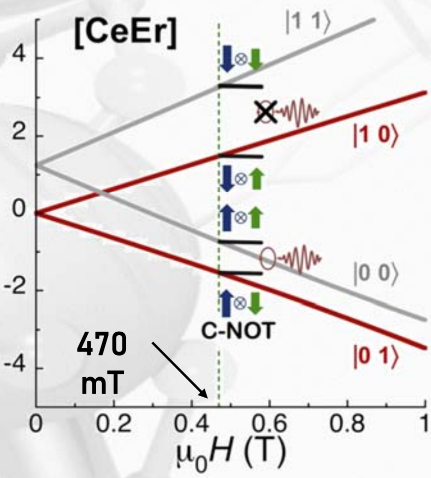
Qubits Weakly Interacting

J. Am. Chem. Soc. **2014**, *136*, 14215

Realization of 2-Qubit Quantum Gates

CNOT Qugate

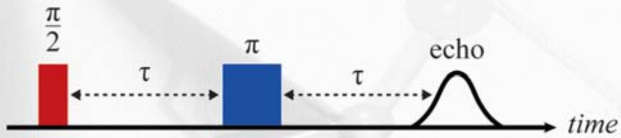




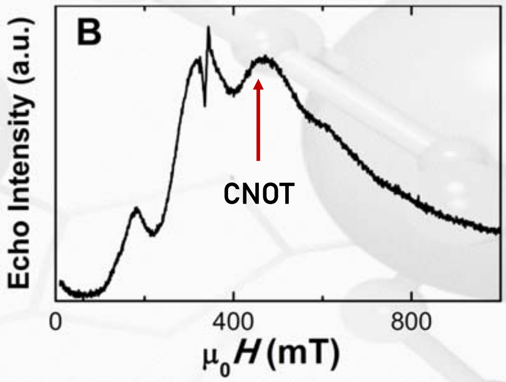
J. Am. Chem. Soc. **2014**, *136*, 14215

Quantum Coherence

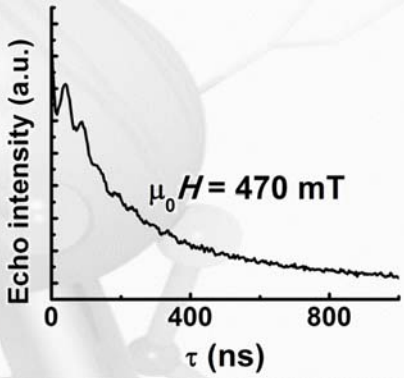
Hahn Echo Sequence



Echo Detected Spectrum, 5K



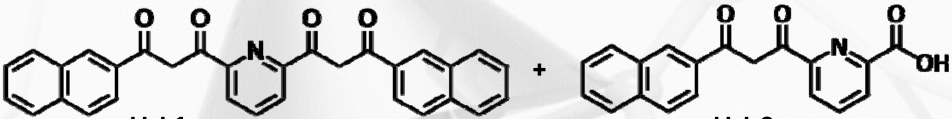
Decay of the CNOT Spin-Echo, 5K



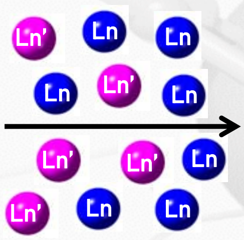
T_2 = 410 ns

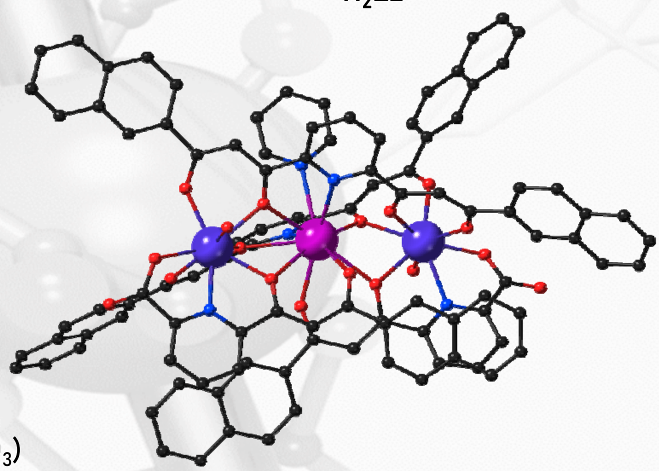
J. Am. Chem. Soc. **2014**, *136*, 14215

Heterometallic [LnLn'Ln] Complexes



H_2L1 H_2L2



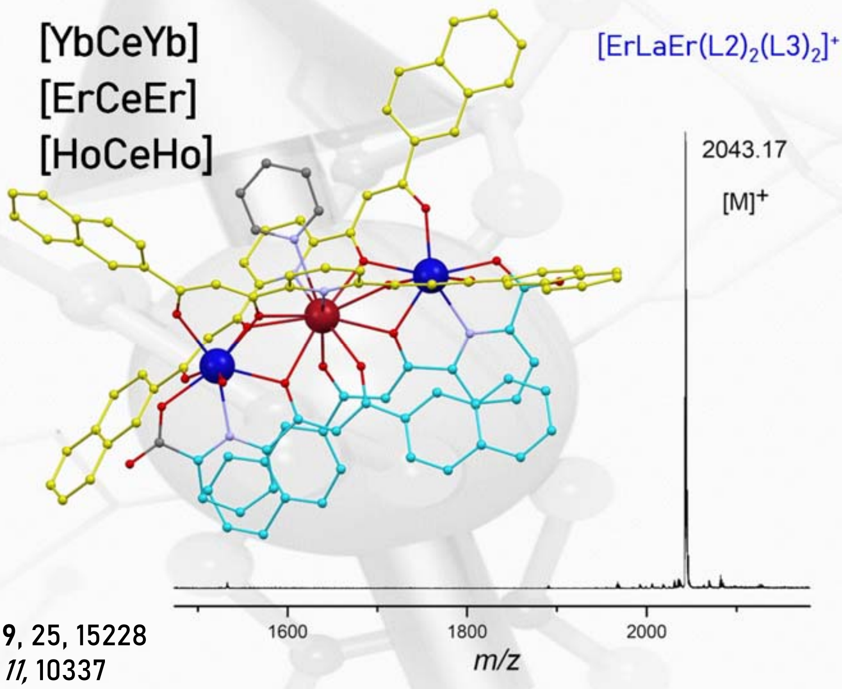


$[Ln_2Ln'(L1)_2(L2)_2(H_2O)_2(py)](NO_3)$

Chem., Eur. J. **2019**, 25, 15228

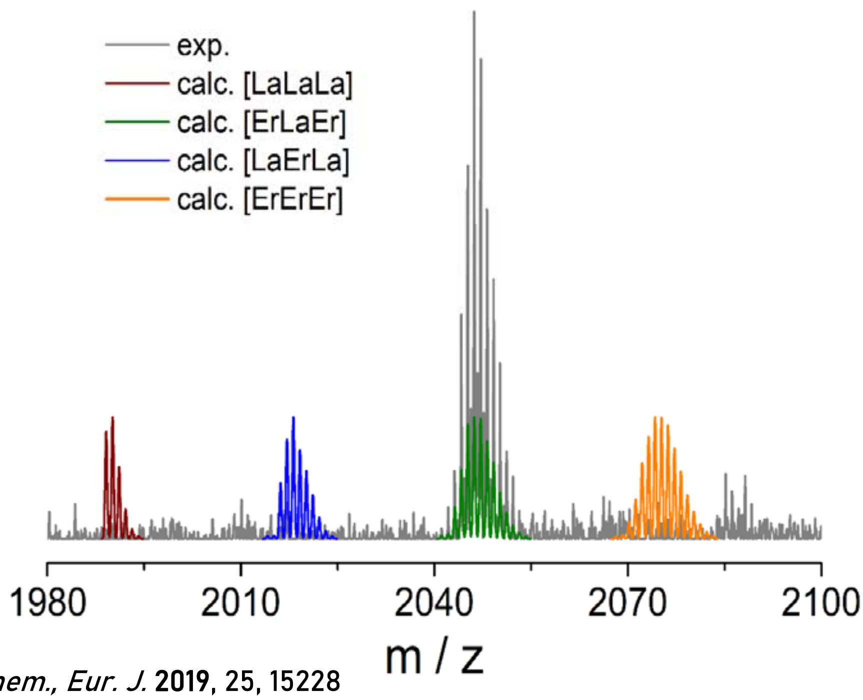
Pure Heterometallic LnLn'Ln clusters

[LuCeLu] [YbCeYb]
[ErLaEr] [ErCeEr]
[ErNdEr] [HoCeHo]
[YbNdYb]
[ErPrEr]
[YbLaYb]
[YbPrYb]
[LuPrLu]
[LuNdLu]
[DyCeDy]



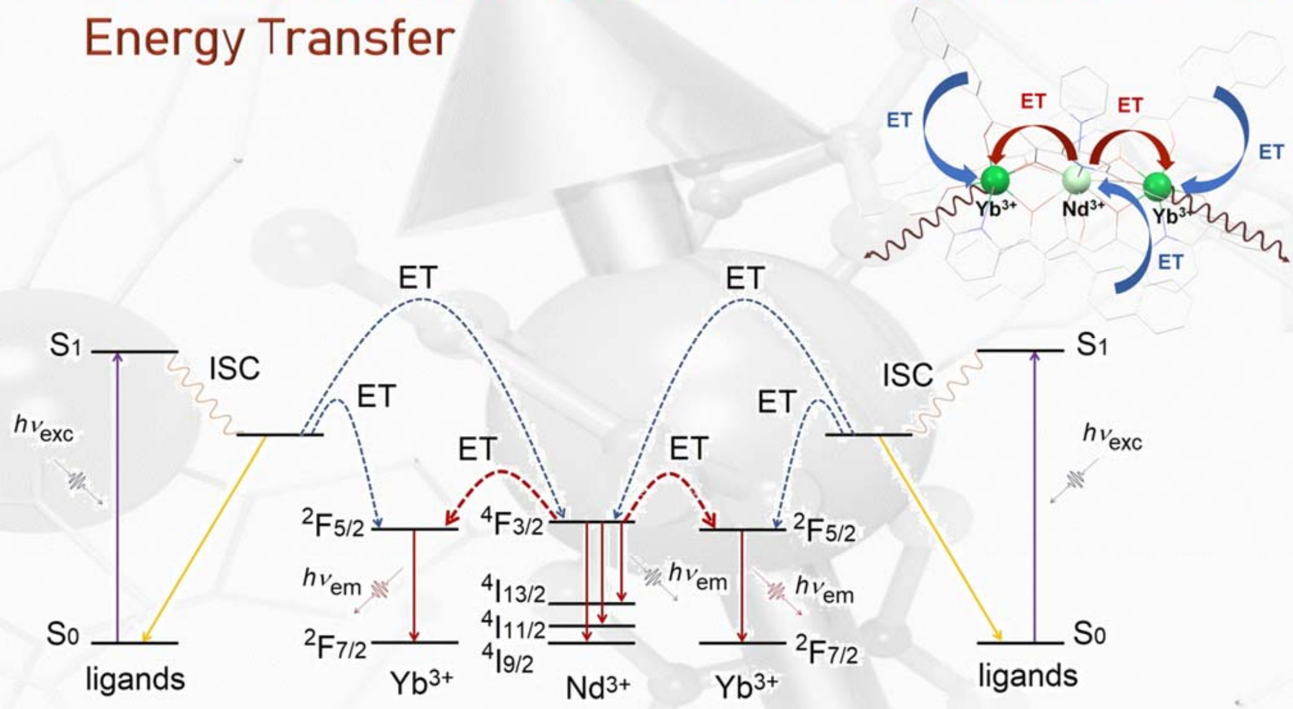
Chem., Eur. J. **2019**, 25, 15228
Chem. Sci., **2020**, *11,* 10337
Chem. Sci., **2022**, *13*, 5574

Metal Distribution in LnLn'Ln clusters



Chem., Eur. J. **2019**, 25, 15228

Distributive Intramolecular Heterometallic Ln-to-Ln' Energy Transfer

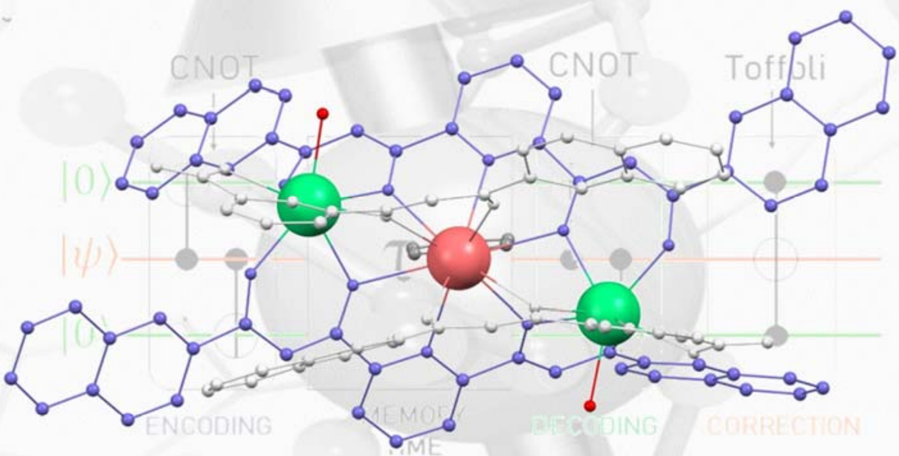


Inorg. Chem. **2023**, *62*, 3106-3115

A Three Qubit Quantum Gate

[ErCeEr]

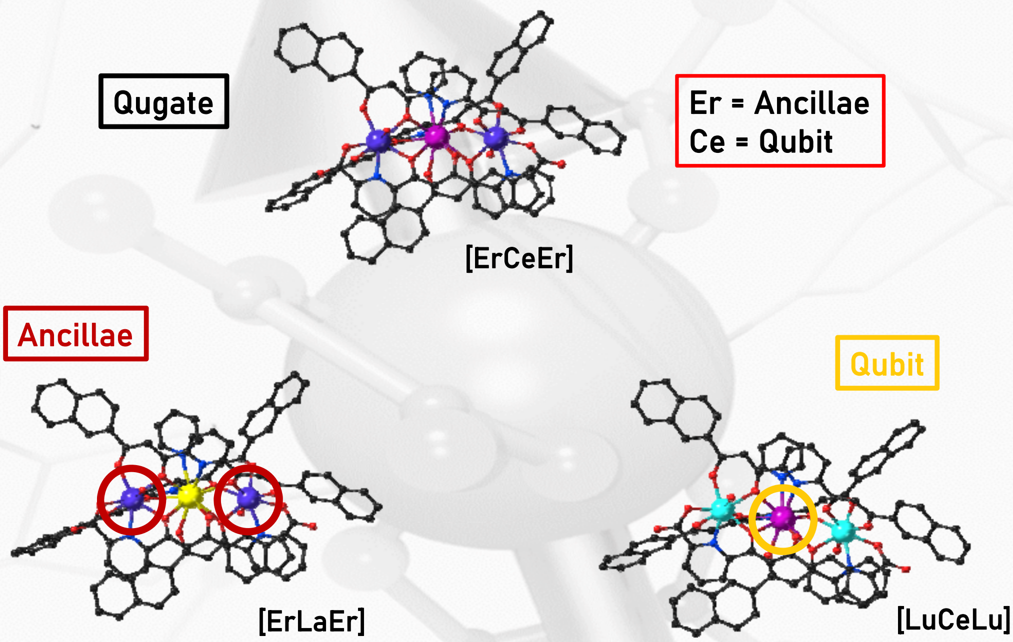
Er(III); $^4I_{15/2}$; L = 6, S = 3/2, J = 15/2
Ce(III); $^2F_{5/2}$; L = 3, S = 1/2, J = 5/2



$$H_0 = \mu_B \sum_i \boldsymbol{S}_i \cdot \boldsymbol{g}_i \cdot \boldsymbol{B} + \boldsymbol{S}_{Er1} \cdot \boldsymbol{J}_{Er1Ce} \cdot \boldsymbol{S}_{Ce} + \boldsymbol{S}_{Ce} \cdot \boldsymbol{J}_{CeEr2} \cdot \boldsymbol{S}_{Er2} + \boldsymbol{S}_{Er1} \cdot \boldsymbol{J}_{Er1Er2} \cdot \boldsymbol{S}_{Er2}$$

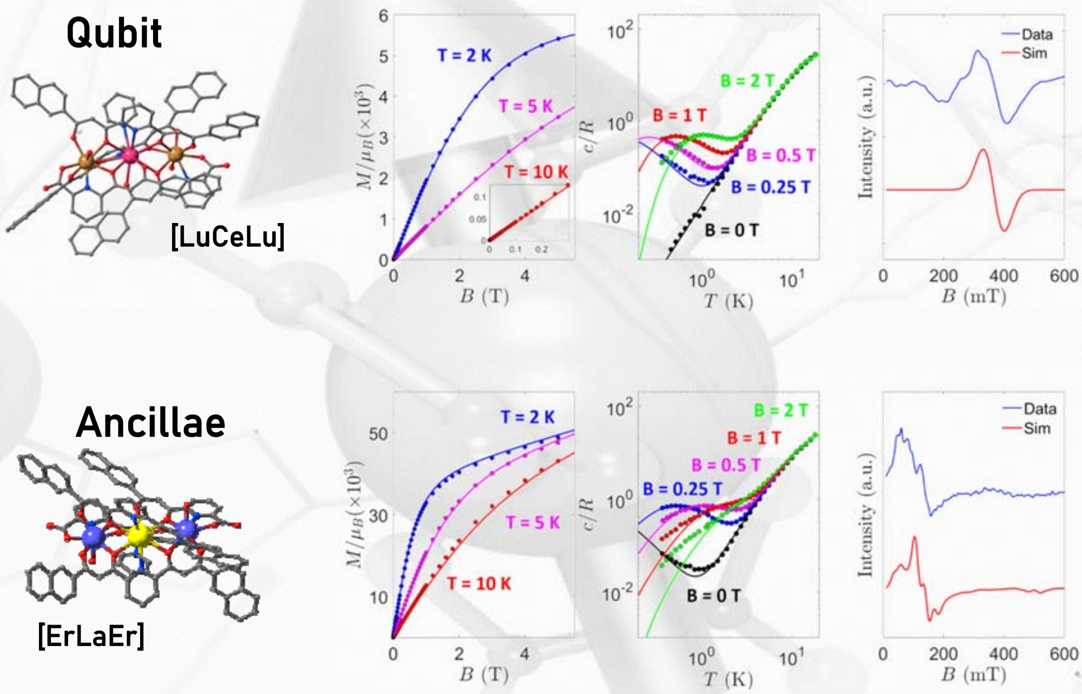
Chem. Sci., **2020**, *11*, 10337

Qubit and Switch Characterization



Chem. Sci., **2020**, *11*, 10337

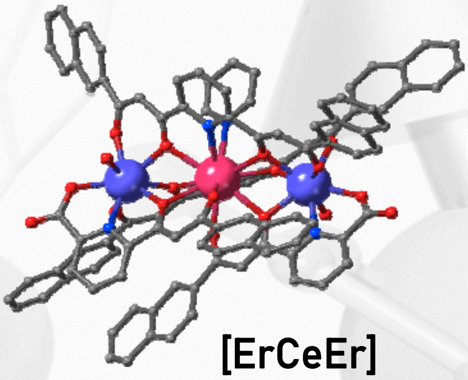
Qubit and Ancillae Characterization

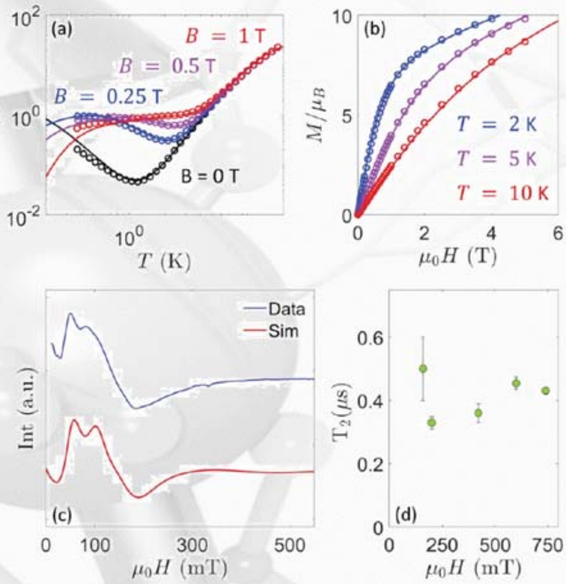


Chem. Sci., **2020**, *11*, 10337

Qubit - Ancillae Interaction

Specific Heat

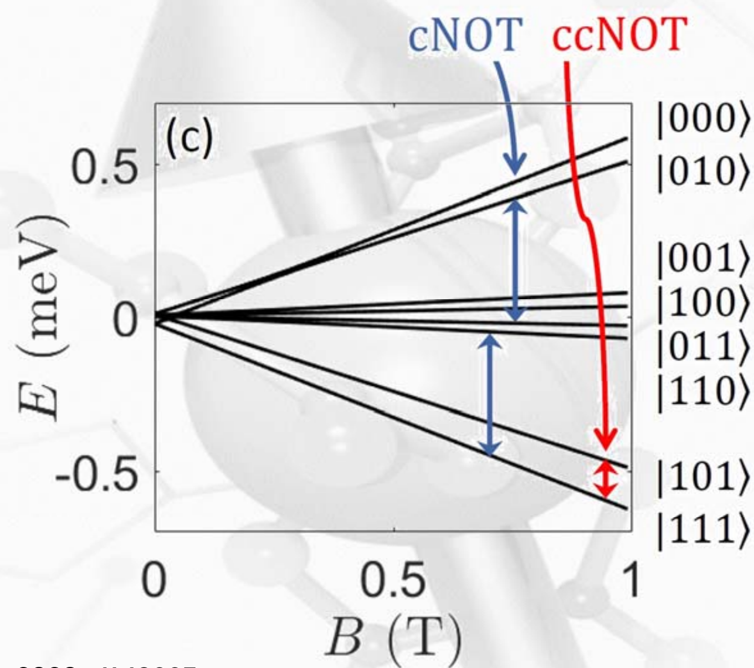




Qubit and Ancillae Interact; J_{ex}/k_B = 0.23 K

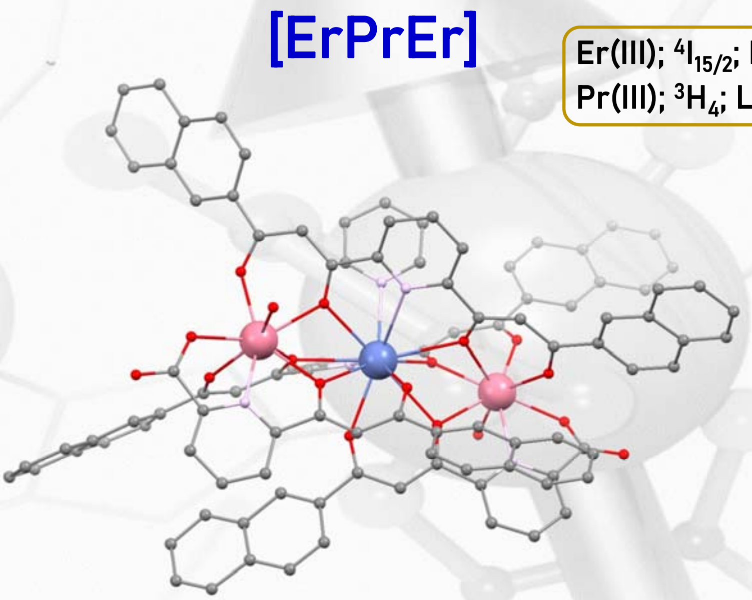
Chem. Sci., **2020**, *11*, 10337

Energy of the Computational Basis



Chem. Sci., **2020**, *11*, 10337

Quantum Coherence and Coherent Control

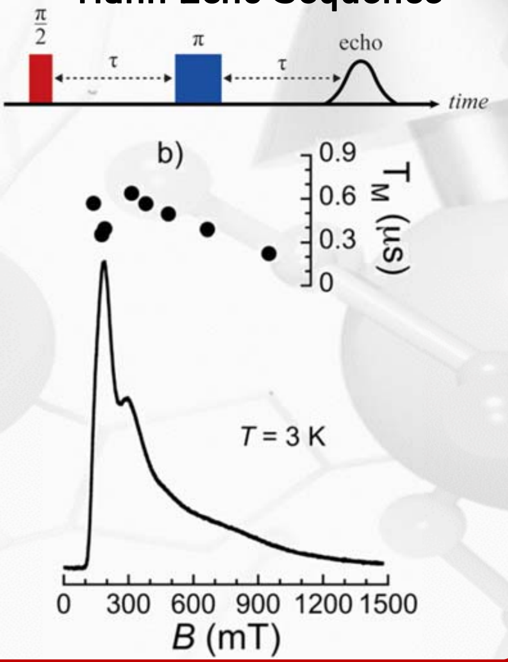


Er(III); $^4I_{15/2}$; L = 6, S = 3/2, J = 15/2
Pr(III); $^3H_4$; L = 5, S = 1, J = 4

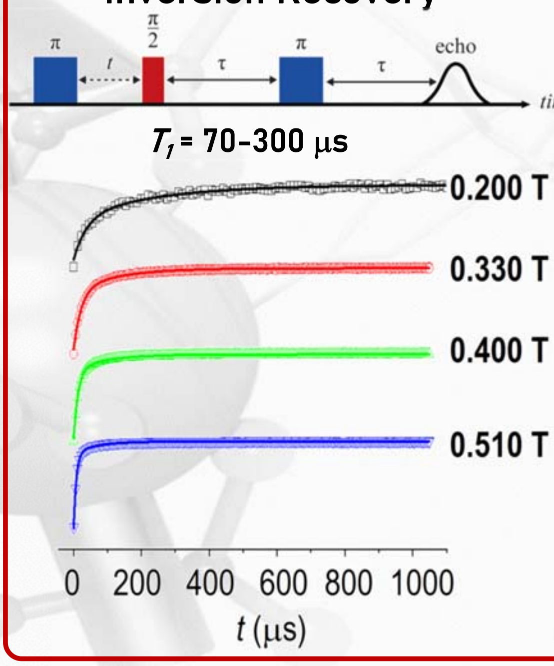
Chem. Sci., **2022**, *13, 5574*

Quantum Coherence (T_1 and T_M)

Hahn Echo Sequence



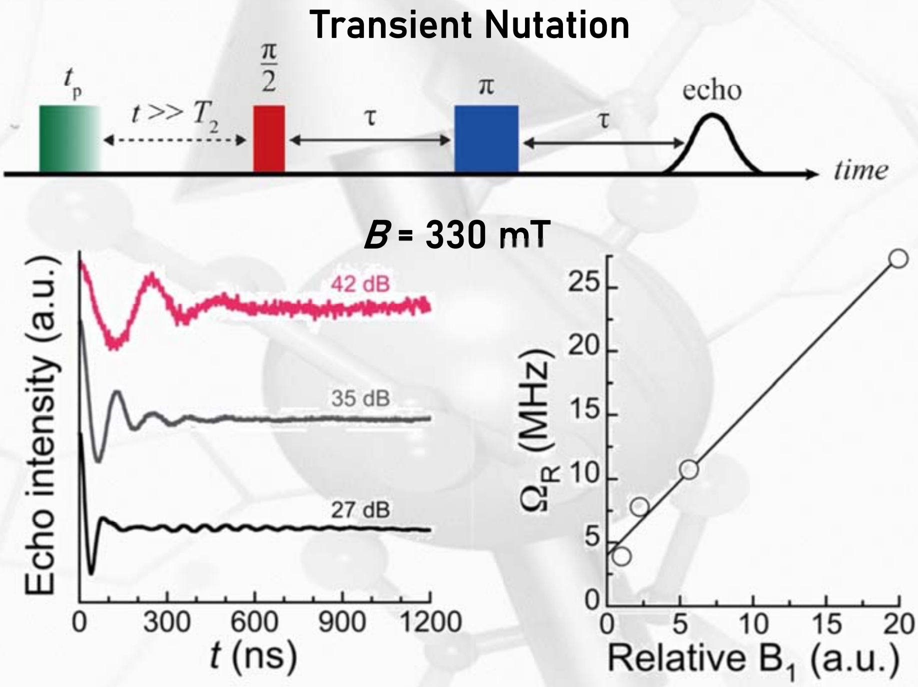
Inversion Recovery



T_1 = 70–300 μs

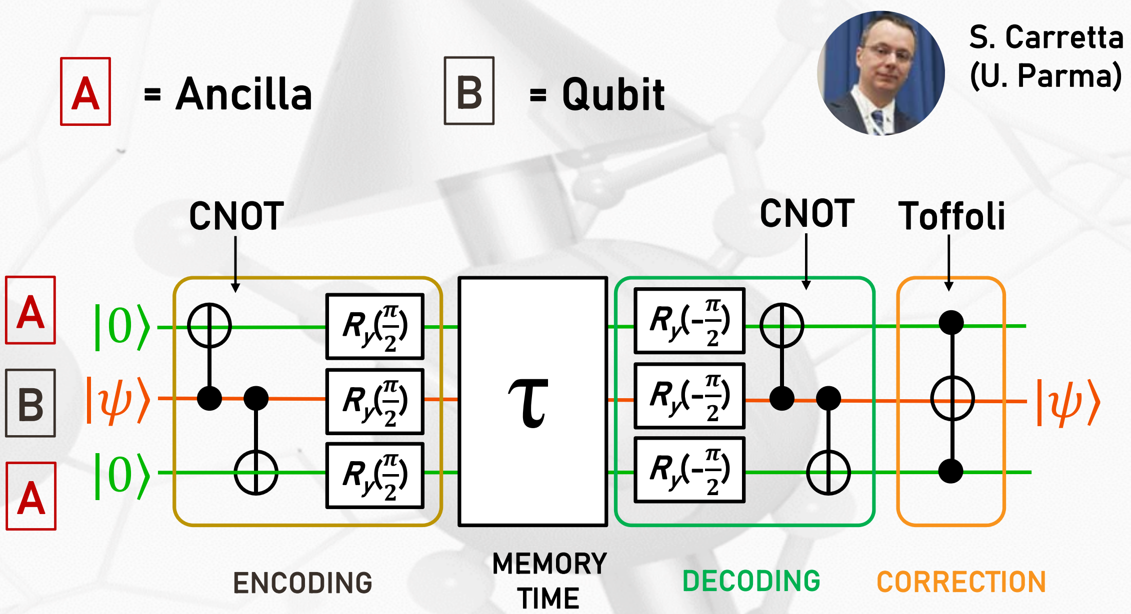
Chem. Sci., **2022**, *13, 5574*

Coherent Control (Ω_R)

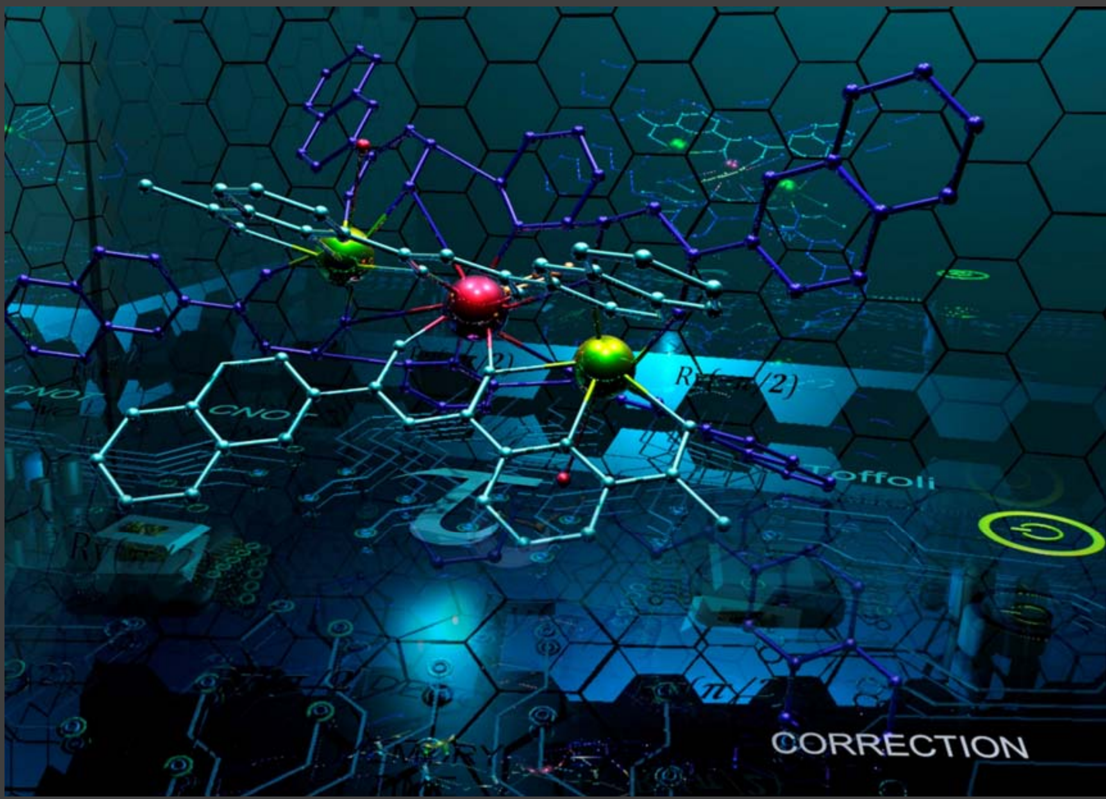


Chem. Sci., **2022**, *13*, 5574

A Qubit with Embedded Error Correction



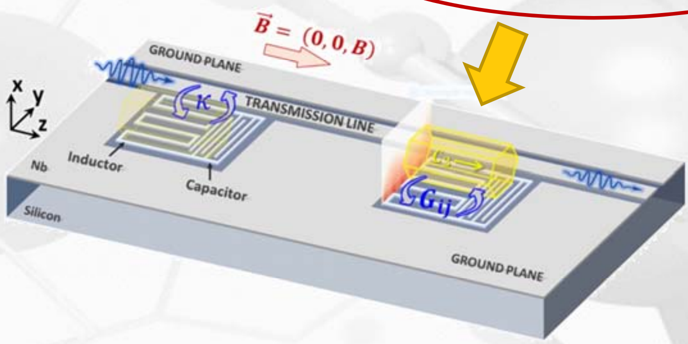
Chem. Sci., **2020**, *11*, 10337

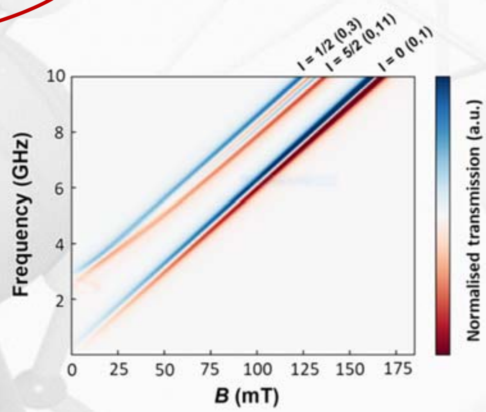


Chem. Sci., **2020**, *11*, 10337

Integration into hybrid architectures: On chip spectroscopy

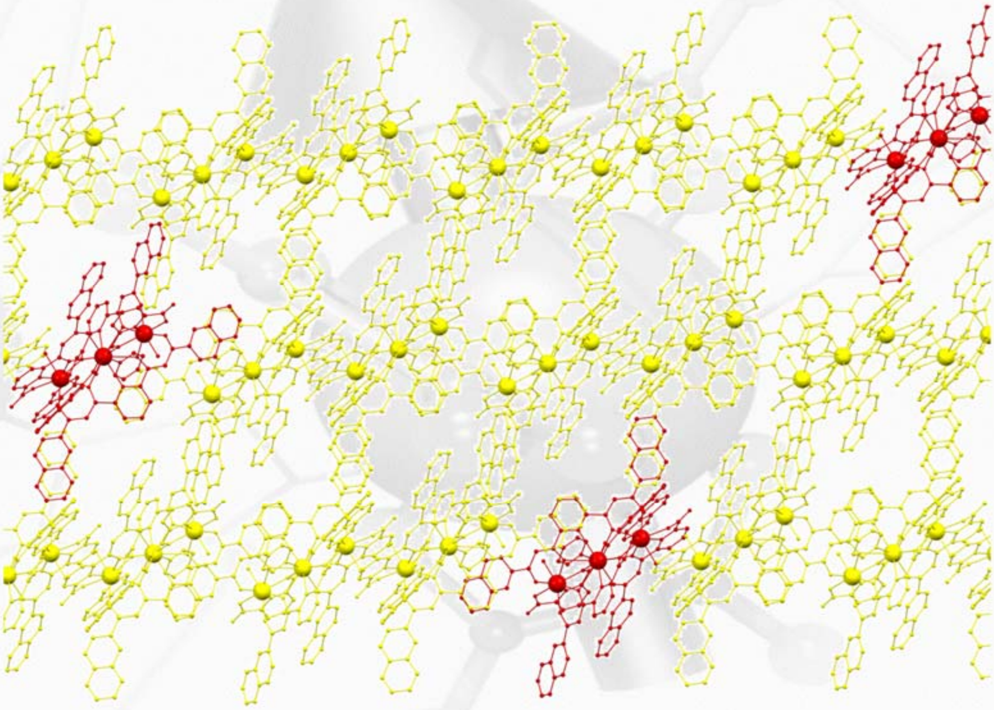
Single crystal of [Lu(trensal)] doped with 7% [^{173}Yb(trensal)]





Luis, Carretta, Piligkos *et al. Communications Physics* 2022, 5

GOAL: Doped [LnLn'Ln] qugates within a diamagnetic single crystal matrix of [LuLaLu]

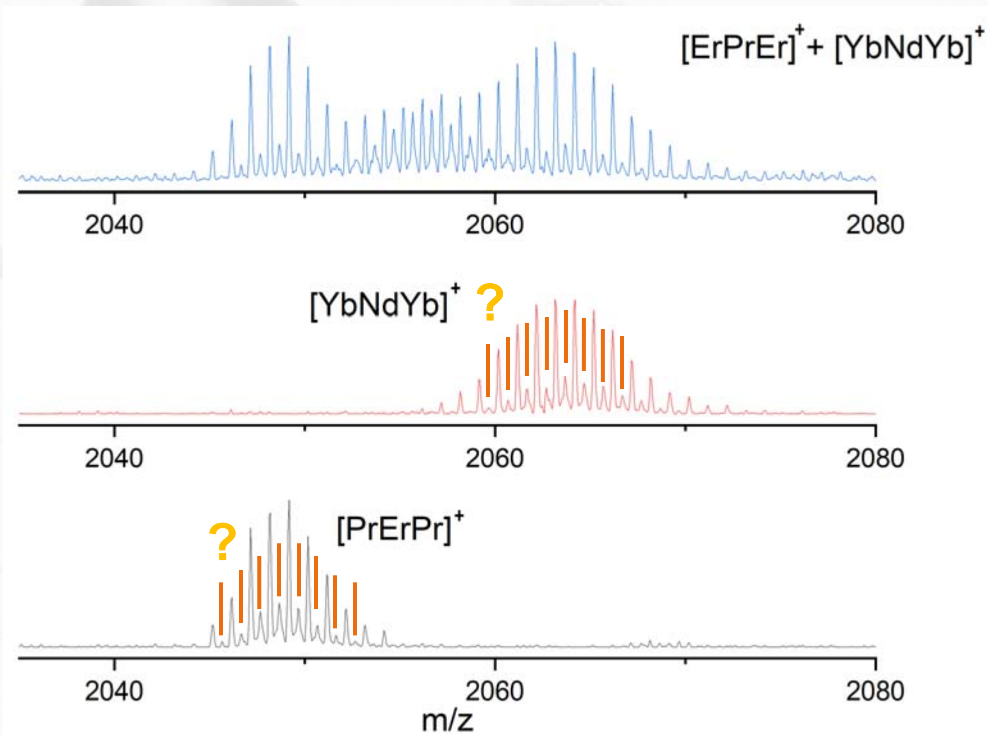


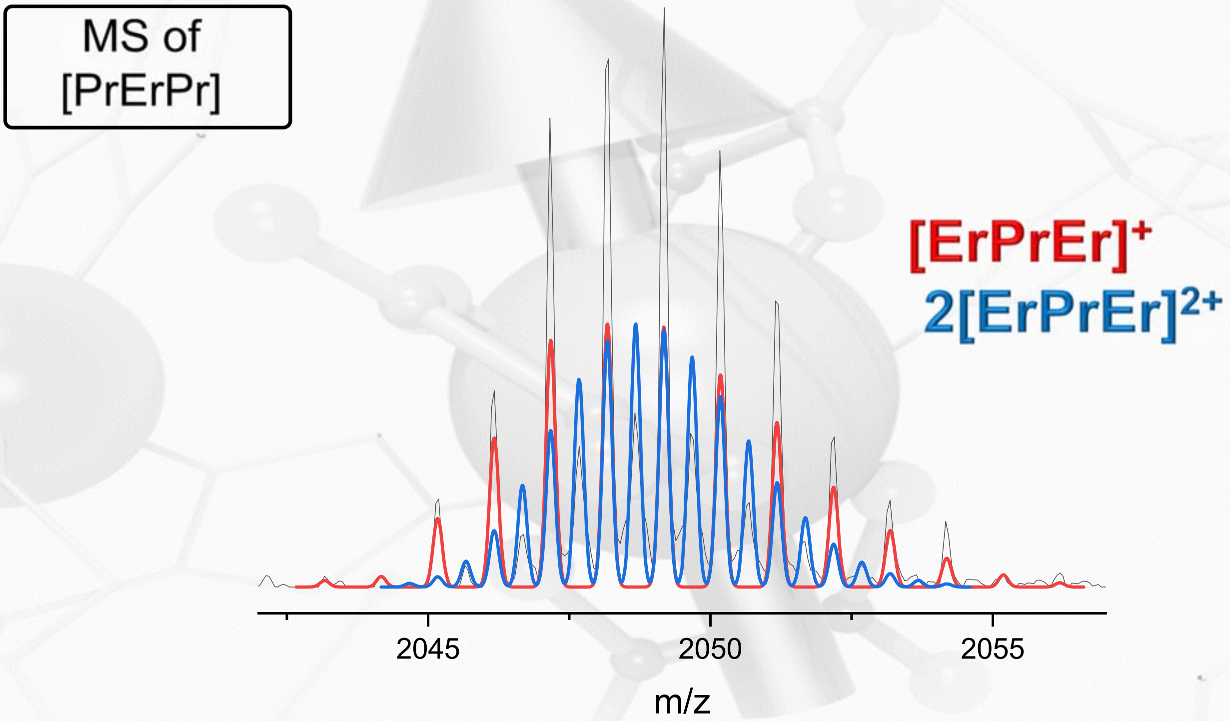
Absence of Metal Scrambling in Solution

MS of a Mixture of [ErPrEr] and [YbNdYb]

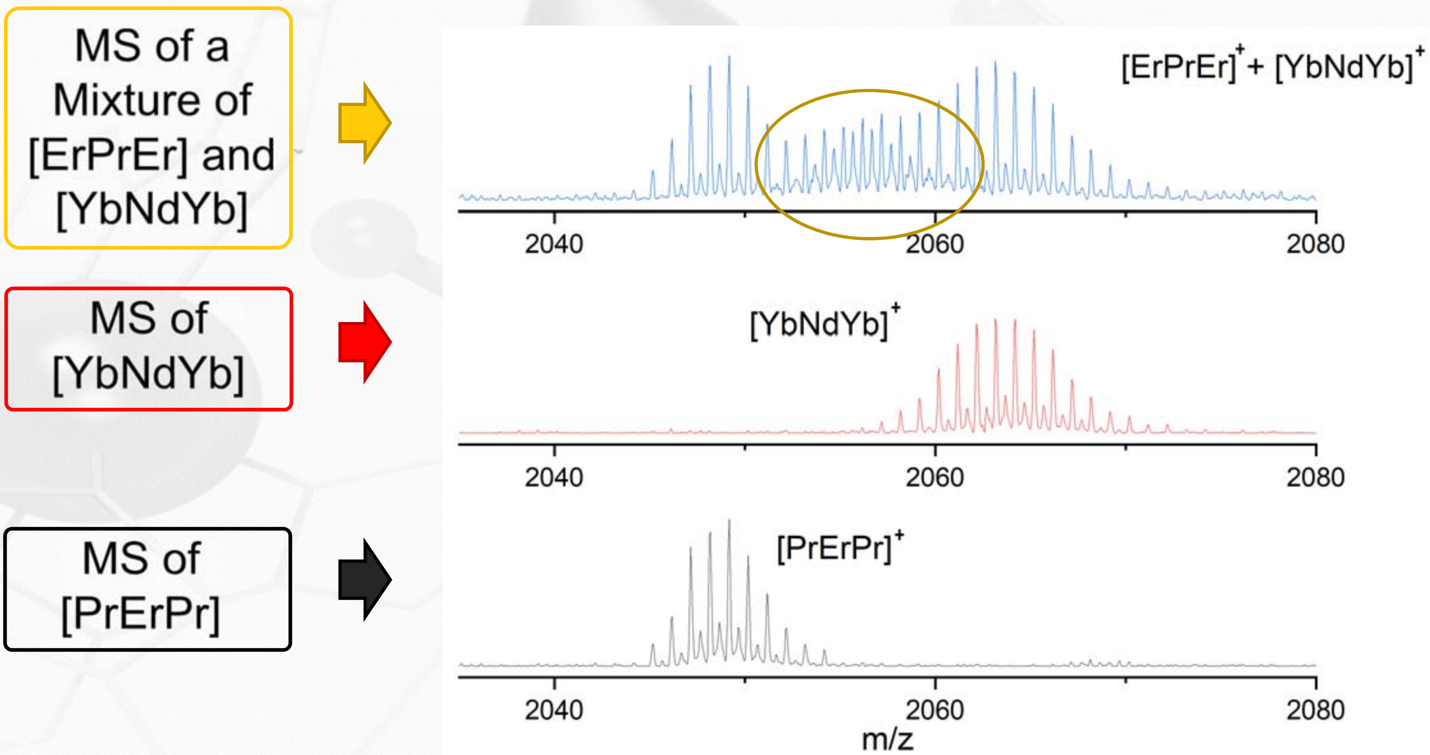
MS of [YbNdYb]

MS of [PrErPr]

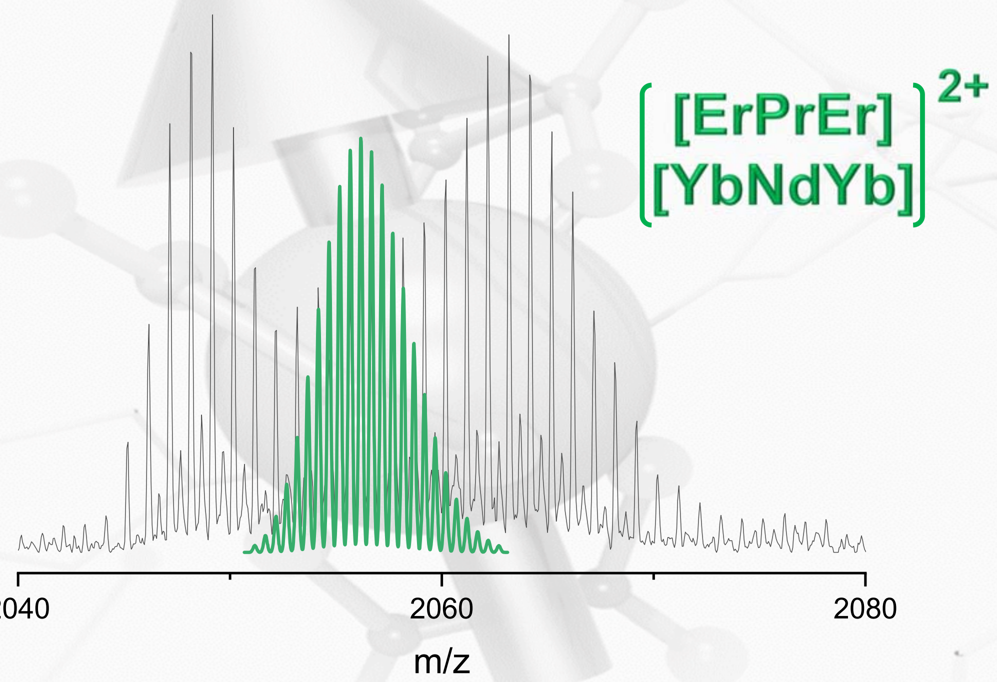




Absence of Metal Scrambling in Solution



MS of a Mixture of [ErPrEr] and [YbNdYb]

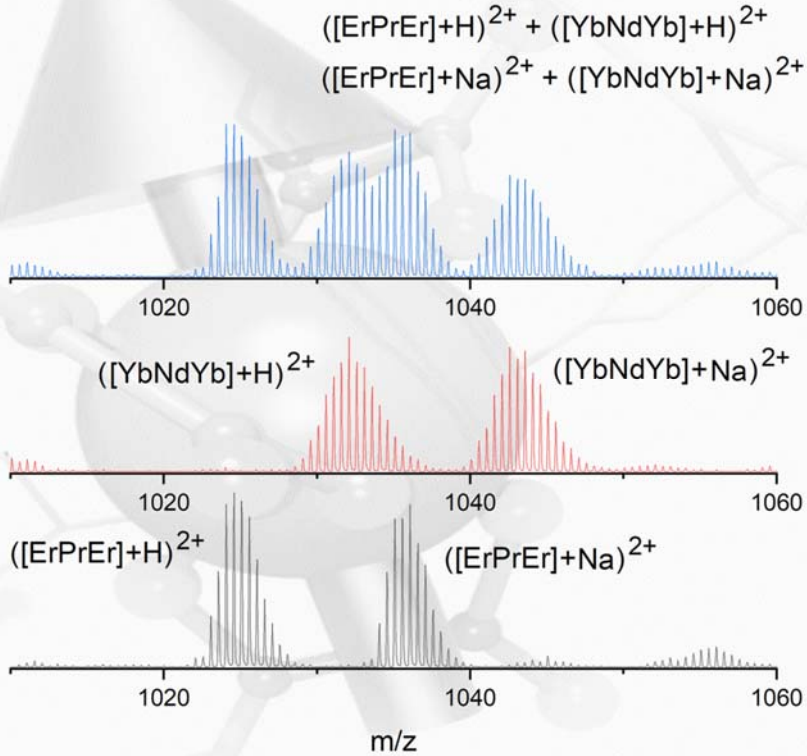


Absence of Metal Scrambling in Solution

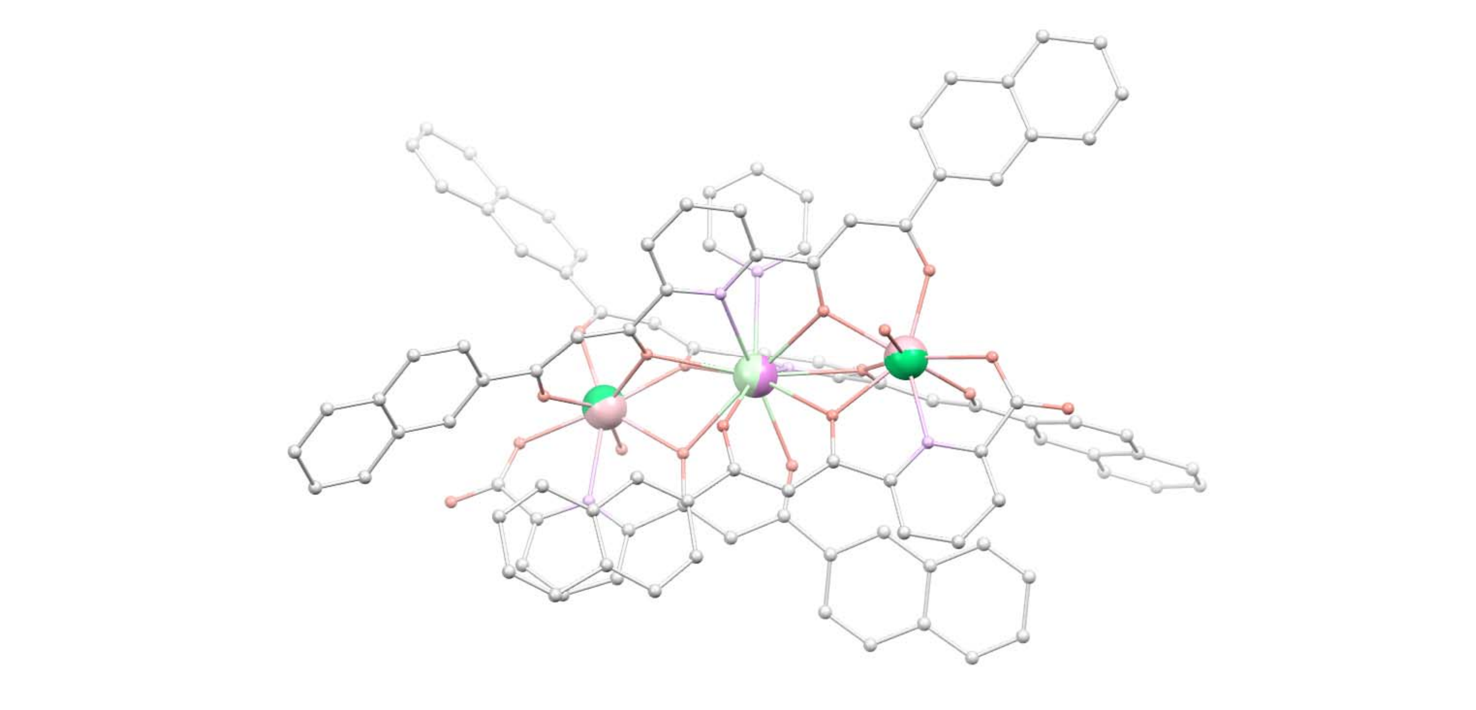
MS of a Mixture of [ErPrEr] and [YbNdYb]

MS of [YbNdYb]

MS of [PrErPr]

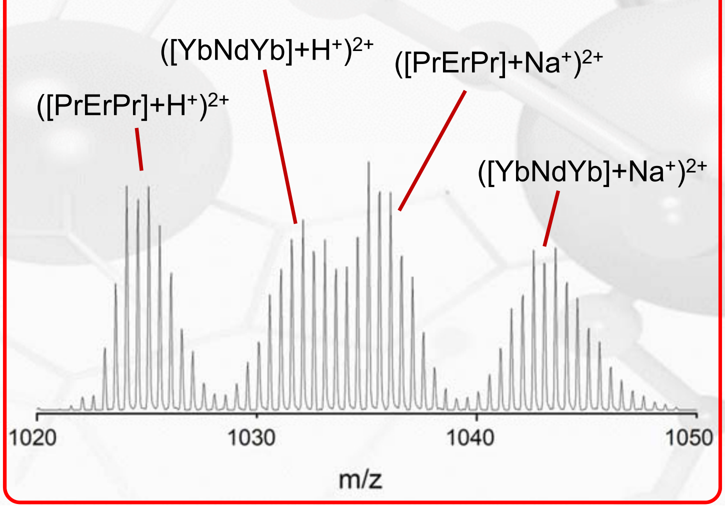


Single Crystals of solution $[ErPrEr]_{0.5}[YbNdYb]_{0.5}$

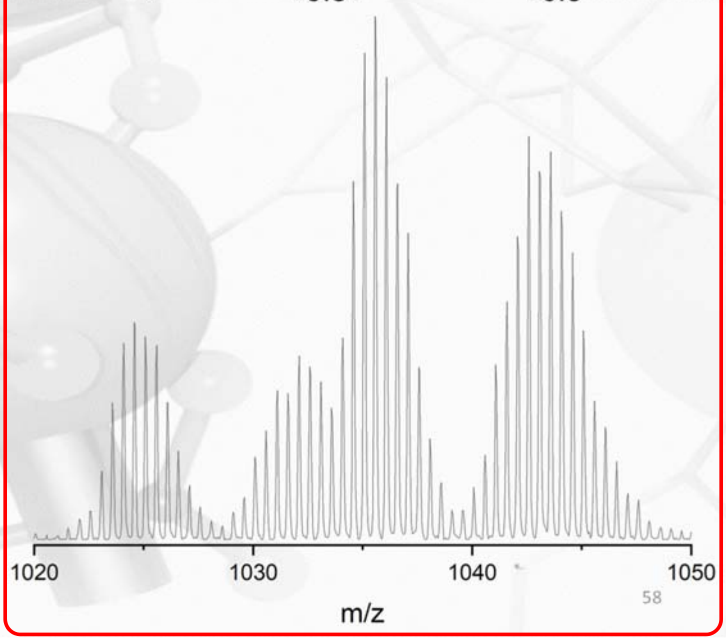


MS of solution of "solid-solution" of [ErPrEr] + [YbNdYb]

MS of a Mixture of [ErPrEr] and [YbNdYb]



MS of crystals of $[ErPrEr]_{0.5}[YbNdYb]_{0.5}$



CONCLUSIONS

1] Ligand Design Provides Entry into Heterometallic Ln complexes

2] **Heterometallic [LnLn']** complexes are a versatile plataform for a wide number of 2-Qubit Qugate designs.
- A C-NOT and SWAP Qugate presented

3] **Heterometallic [LnLn'Ln]** complexes provide possible realizations of 3-Qubit Qugates.
-A Quantum Error Protection Device

Acknowledgements

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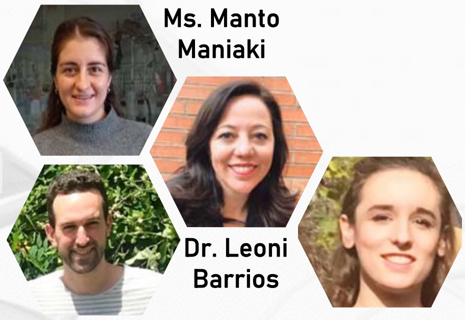

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SUMO; Scaling Up quantum computation with MOlecular spins

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