

Enhancing intramolecular ferromagnetic coupling in Tetrathiafulvalene-Nitronyl Nitroxide-based compounds through Spin Polarization mechanism



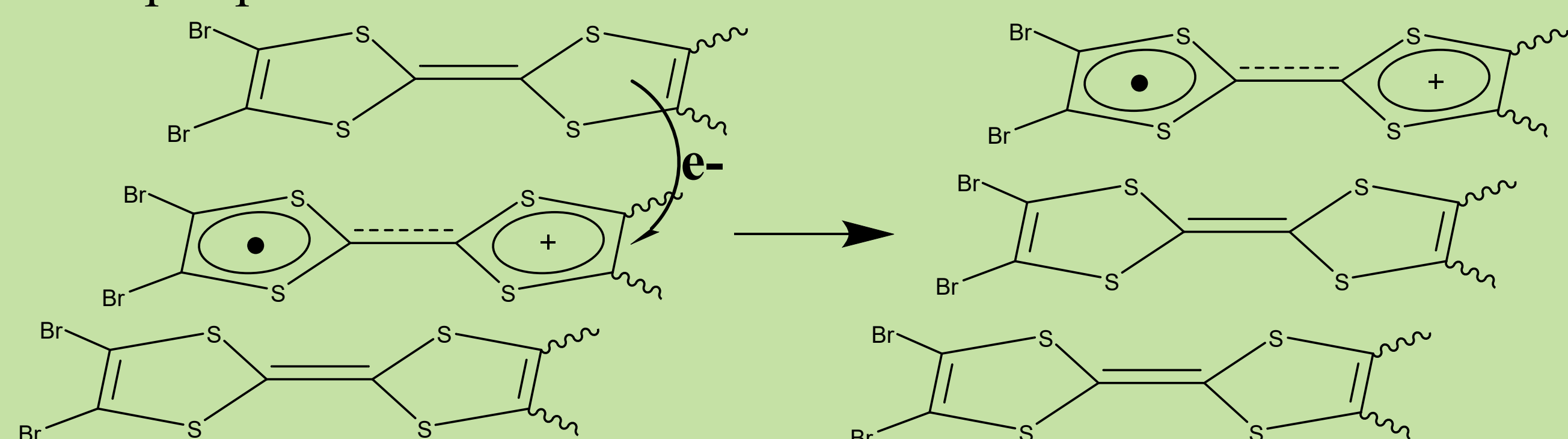
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1. INTRODUCTION

► Organic semiconductors are crucial to advance next-generation spintronic devices, yet enable novel phenomena such as **magnetoresistance (MR)**. This research was inspired by the giant negative MR reported by first time in a purely organic BTBN crystal^[1].

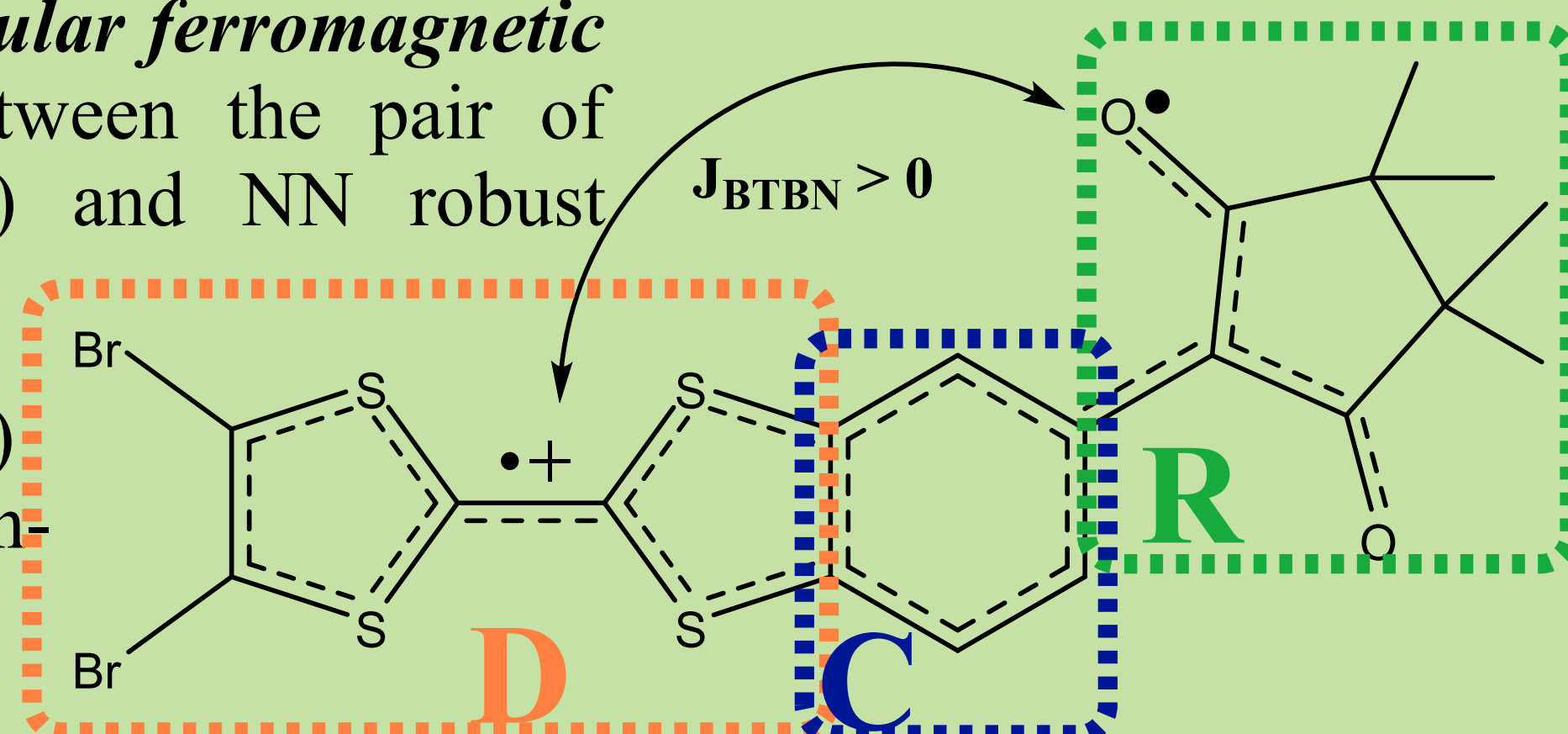
► It is also known that oxidation occurs at the HOMO of TTF unit, rather than at the SOMO of NN radical. Thus, upon hole injection, MR results from the **interplay between magnetism and conductivity**^[2] in BTBN⁺ diradicals:

✓ **Intermolecular hole migration** along the π -stacking direction of spin-polarized TTF donors.



✓ **Strong intramolecular ferromagnetic (FM) coupling** between the pair of spins in TTF⁺ (D) and NN robust radical (R).

A phenyl coupler (C) mediates this through-bond interaction



The study assesses the performance of 20 newly *in silico*-designed derivatives, aiming for larger FM exchange couplings $J_{DjCjRk} > J_{BTBN}$.

J exchange coupling values determine the quality of the derivatives.

COMPUTATIONAL DETAILS

$|\Psi\rangle$ **Theory:** Noodleman solutions to the Heisenberg Hamiltonian at zero field assuming a complete overlap

Computation: DFT (U-B3LYP/6-311+G(d,p) level, vacuum).

3. CONCLUSIONS

- The D4 donor performs better than its TTF⁺ (D1) precursor
- Only the NN (R1) leads to a triplet ground state in the Rk set of radicals.
- Diatomic couplers C2-C4 and -OH group in C9 also produce larger $J_{DjCjRk} > J_{BTBN}$ ($\forall j \in \{2,3,4,9\}$) as desired

2nd generation of *in silico* designed enhanced E1, E2, E3

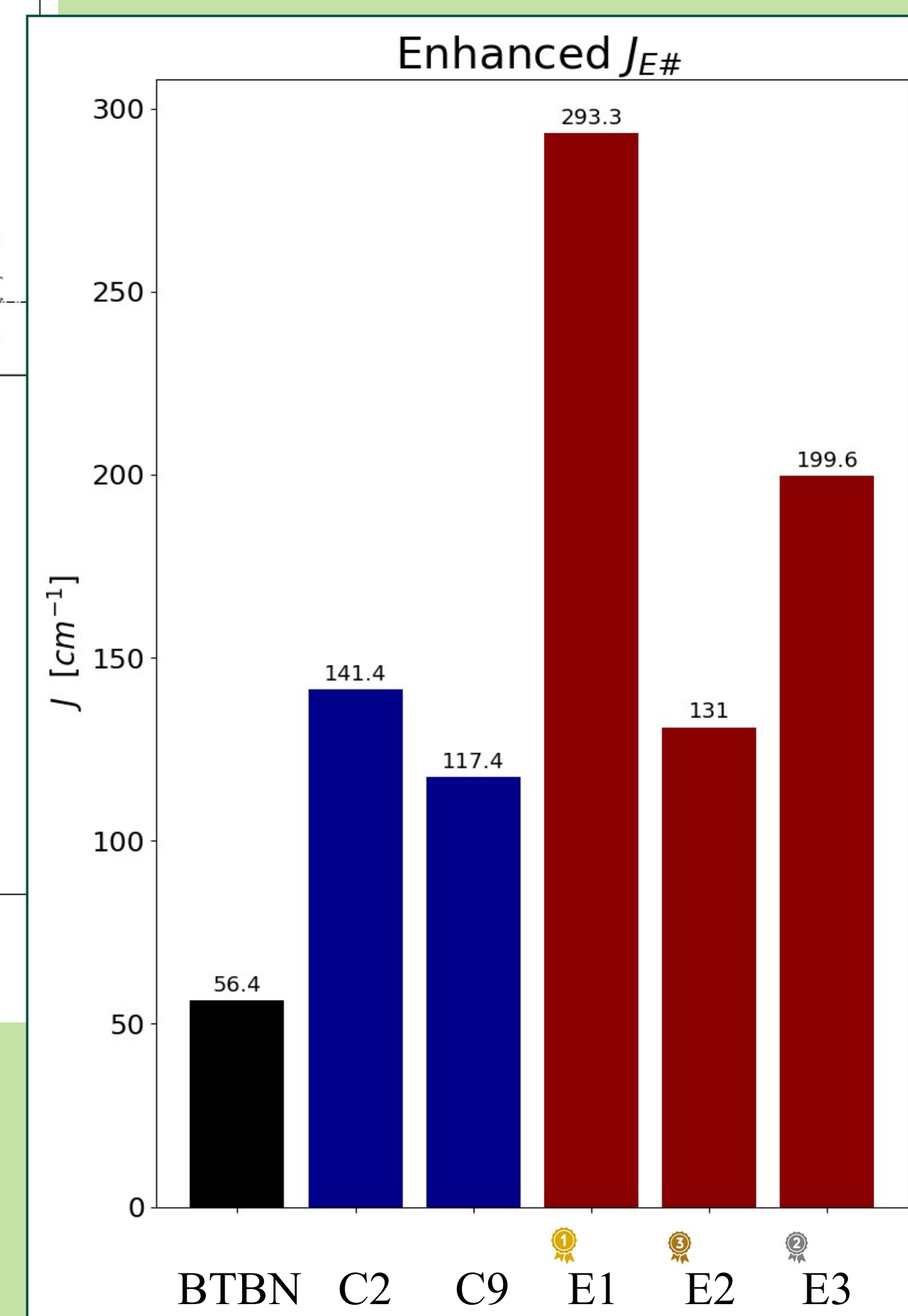
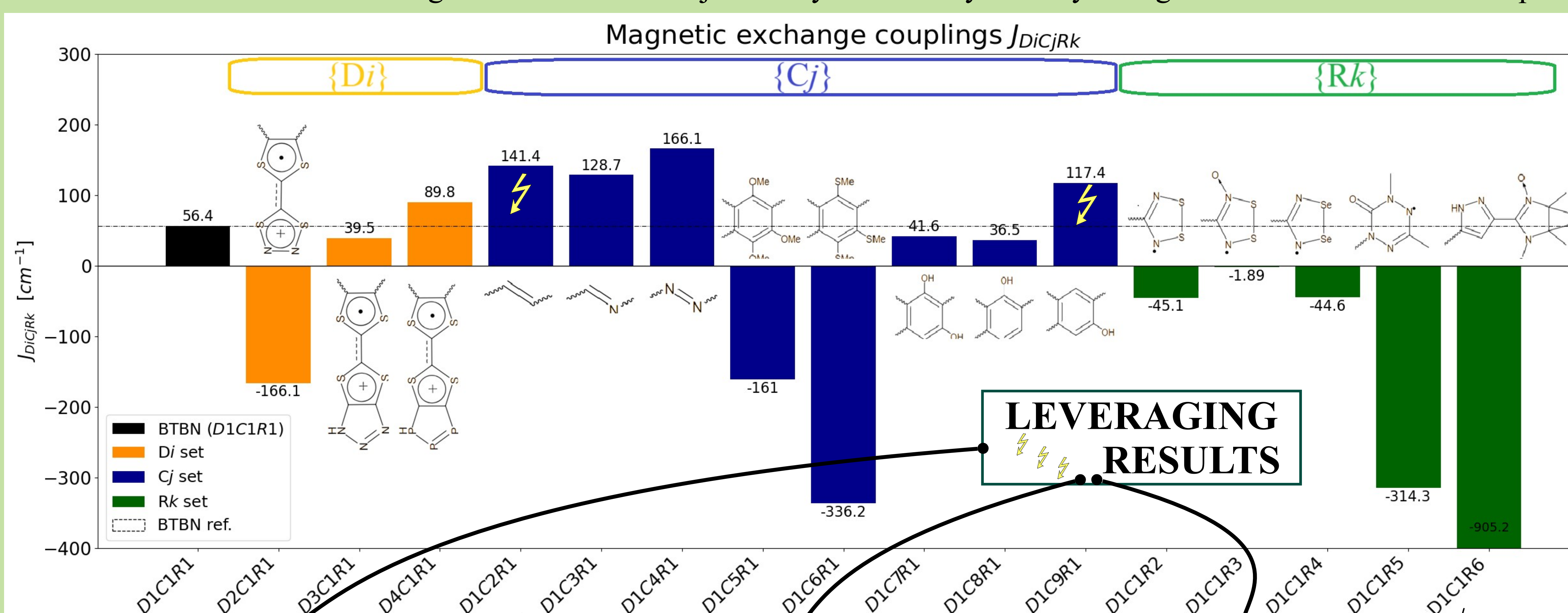
$$J_{E1} > J_{E3} > J_{E2} > J_{BTBN}$$

E1 and E3 are the most promising candidates for enhanced magnetism ... and may boost MR?

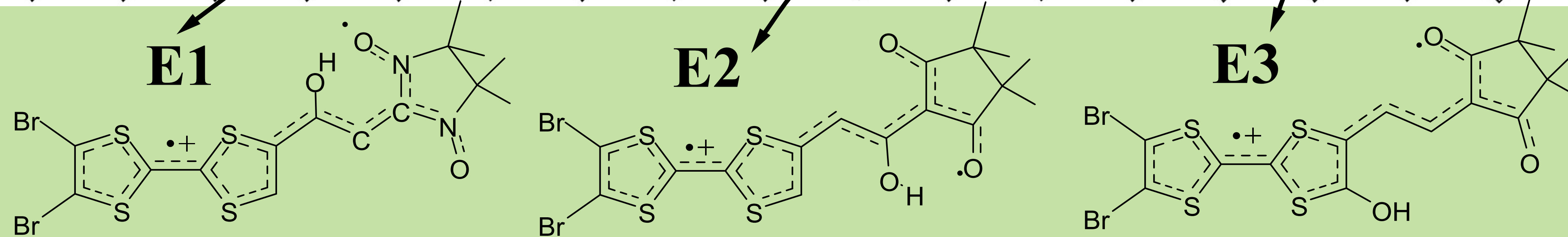
The larger spin-polarized the coupler is in a given state, the more stabilized this is → it becomes the ground state and determines the magnetic properties

2. RESULTS

3 sets of *in silico* designed structures: Di-Cj-Rk to systematically identify changes made on each donor-coupler-radical parts, respectively.



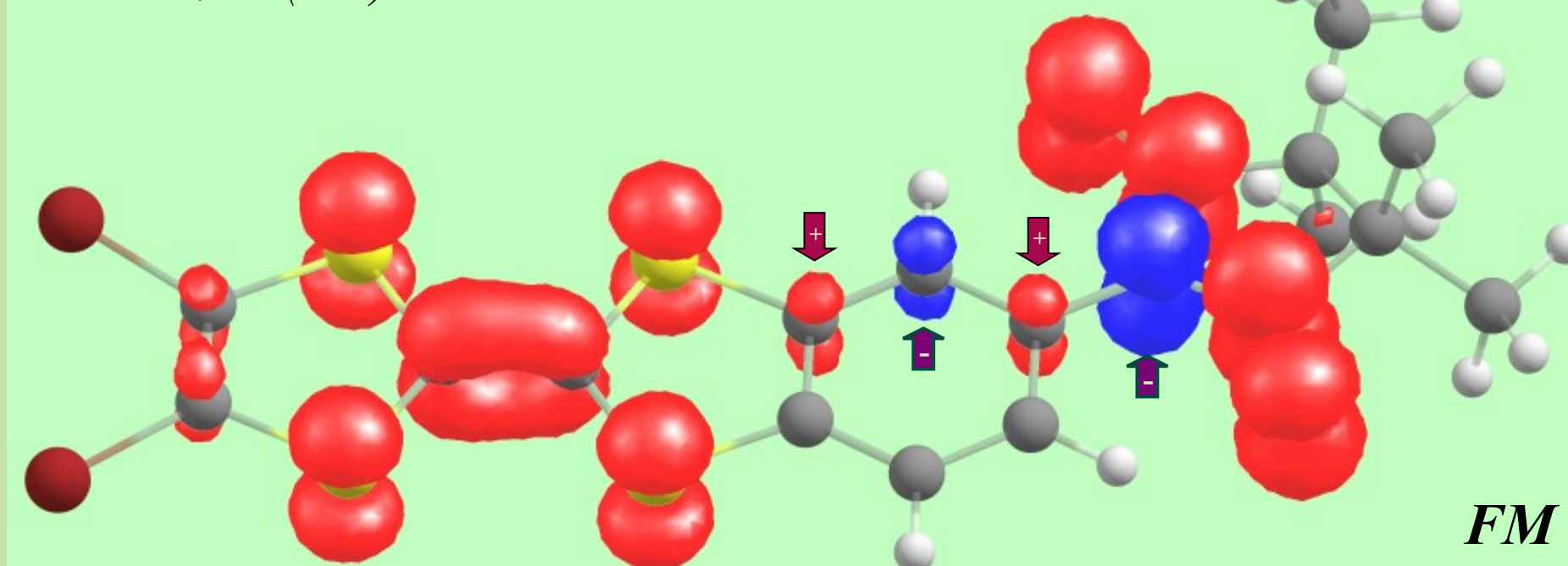
LEVERAGING RESULTS



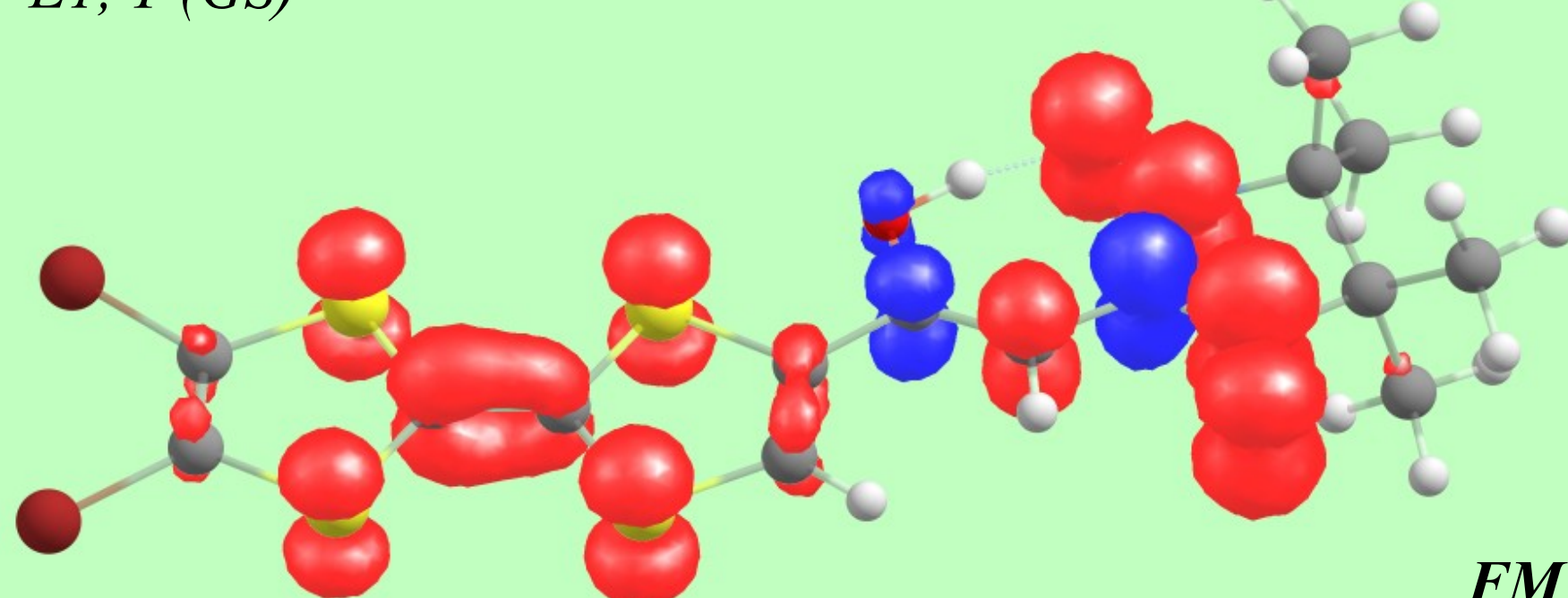
Larger atomic spin densities are found in magnetically-enhanced E# structures, in agreement with the calculated J_{DjCjRk} couplings. Spin polarization (SP) mechanism benefits from larger alternating spin density on coupler, which stabilizes a T/S ground state (GS) depending on magnetic response being either FM/AFM.

We found that SP in BS-S GS favours AFM, and SP in T GS favours FM:

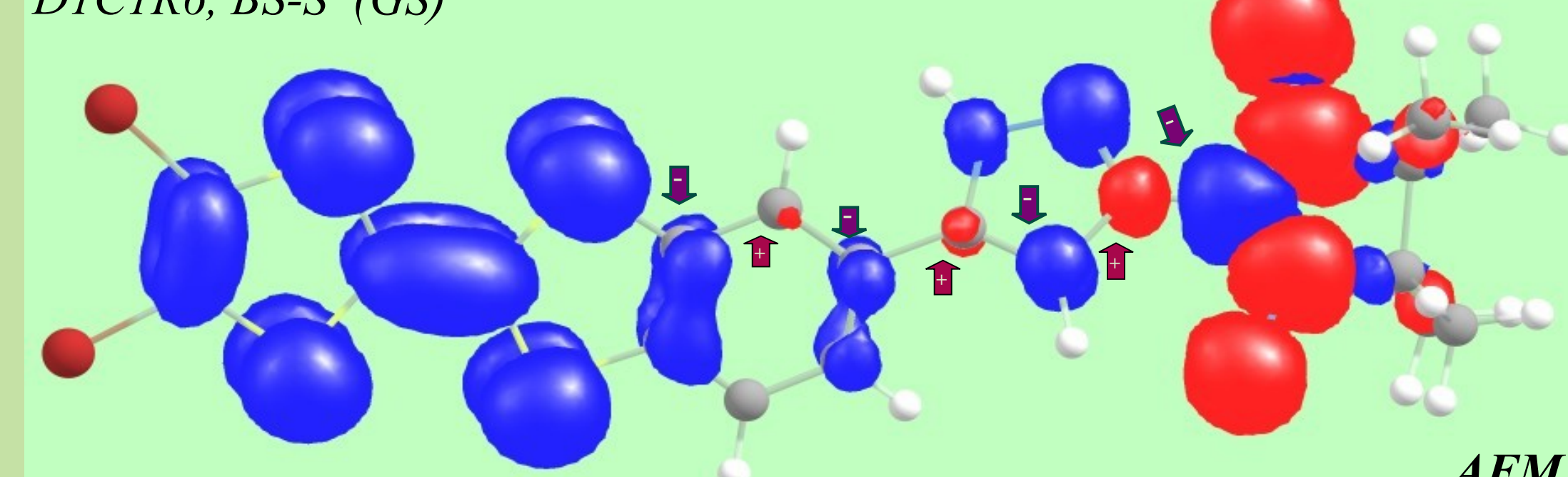
BTBN, T (GS)



E1, T (GS)



D1C1R6, BS-S (GS)



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References

- [1]- H. Komatsu, M. M. Matsushita, S. Yamamura, Y. Sugawara, K. Suzuki, T. Sugawara, *J. Am. Chem. Soc.* 2010, 132, 4528.
- [2]- T. Sugawara, H. Komatsu, K. Suzuki, *Chem. Soc. Rev.*, 2011, 40, 3105-3118

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