Project B5: Rational design with input from DFT calculations and preparation of coordination polymer-based quantum magnets

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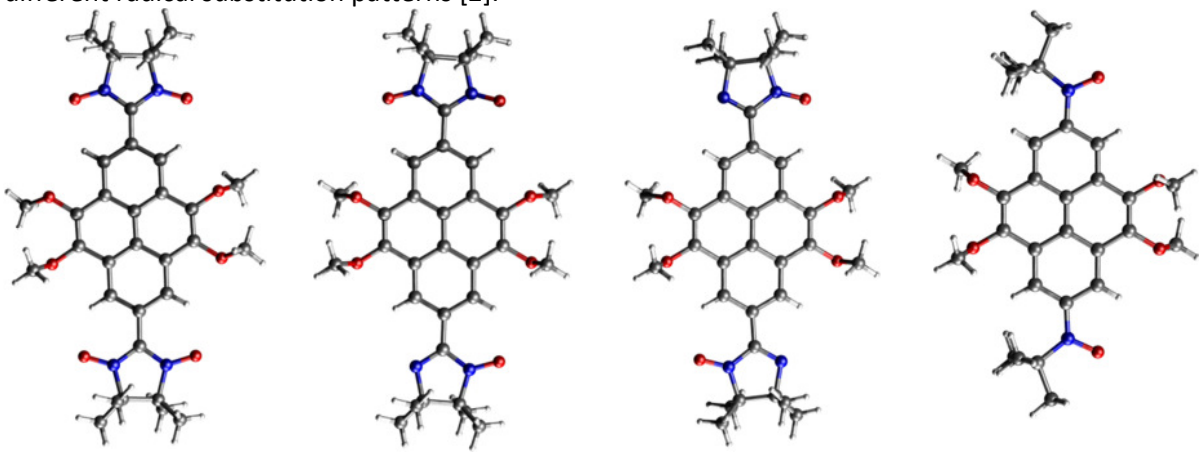
Spin-dimer systems composed of closely-spaced pairs of spin S=1/2 carrying entities, have been used as model systems for exploring critical phenomena under well-controlled conditions. Prominent examples include the Bose-Einstein condensation (BEC) of magnetic excitations in three-dimensionally coupled dimer systems and the Luttinger liquid behaviour in quasi-one-dimensional materials. We are using the self-assembly of molecular building blocks for the rational development of solid BEC materials. The following design principles serve as a useful reference: (i) The intra dimer coupling constant *Jintra* needs to be significantly stronger than any of the intermolecular coupling constants *Jinter*. (ii) On the other hand, *Jintra* has to be small enough to allow for the use of laboratory-scale magnetic instrumentation to moderate the spin gap to such an extent that the Sz = 1 state is adopted by a significant number of spin pairs. (iii) The molecular building blocks must allow an easy and extensive modification of their substitution pattern in order to provide the set-screws for an adjustment of *Jintra* and *Jinter*.

Research Highlight

The magnetic exchange interactions in anti-ferromagnetically coupled biradicals depend on the distance and type of the radical moiety as well as π-conjugated system. Herein we present the systematic tuning of exchange interactions through the conjugated bridge by varying the radical moieties [1,2]. An intriguing case is made for the tetramethoxypyrene (TMP) bridge and its four different radical substitution patterns [2].



TMPNN **TMPmix** **TMPIN** **TMPNO**

Scheme 1: The crystal structures of tetramethoxypyrene bridged biradicals.

These are the first examples of pyrene based neutral biradicals. The fine tuning of magnetic exchange interactions was achieved by changing the radical moieties. The experimental coupling constant (J_{exp}) values are well in accordance with the theoretical ones (J_{calc}).

[1] Mostovich, E.A., Borozdina, Y, Enkelmann, V., Removic-Langer, K., Wolf,B., Lang, M., Baumgarten, M. Planar Biphenyl Bridged Biradicals as Building Block for the Design of Quantum Magnets *Crystal Growth &Design* **2012**, *12*, 54-59. (Doi: 10.1021/cg201224g)
[2] Ravat, P.; Ito, Y.; Gorelik, E.; Enkelmann, V.; Baumgarten, M., Tetramethoxy-Pyrene Based Biradical Donors with Tunable Physical and Magnetic Properties, *Org. Lett.* **2013**, *15*, 4280-4283.(DOI:)