Mechanochemical improvement of Norbornadiene-based molecular solar- thermal systems performance

M. Nucci[1], M. Marazzi[1,2] and L. M. Frutos[1,2]

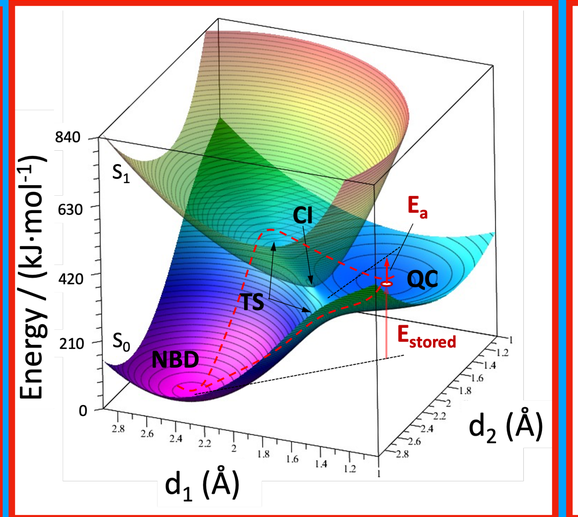
[1]Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Universidad de Alcalá, Ctra. Madrid-Barcelona Km. 33,600, E-28805 Alcalá de Henares (Madrid), Spain

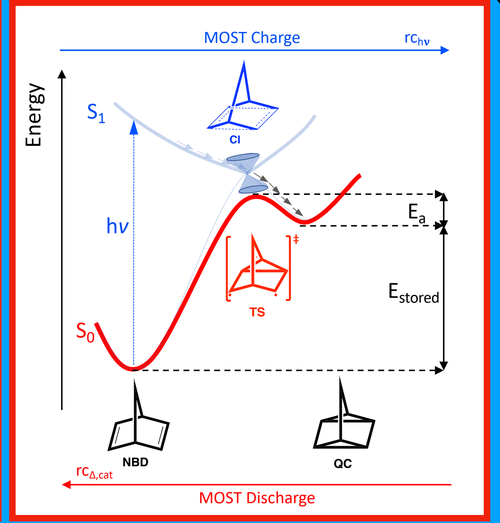
[2] Chemical Research Institute "Andrés M. del Río" (IQAR), Universidad de Alcalá, E-28871 Alcalá de Henares (Madrid), Spain

martina.nucci@uah.es

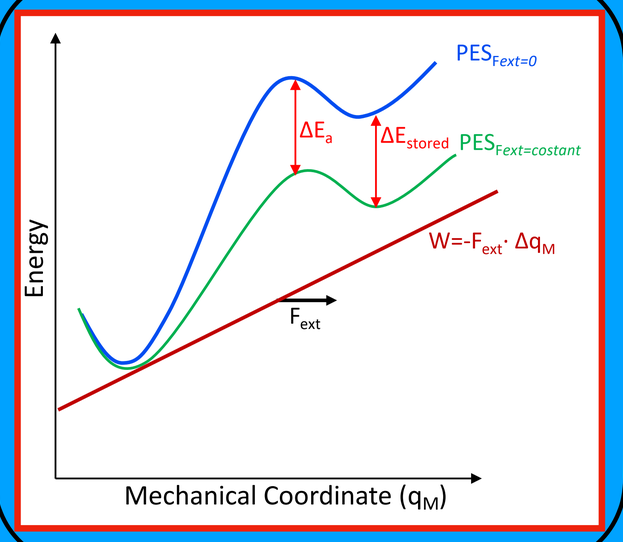
The Norbornadiene-Quadricyclane system:

- ✓ Low molecular weight (92.14 g/mol) and high storage enthalpy (96kJ/mol)
- ✗ The absorption of the system is well above in energy with respect to the solar radiation spectrum

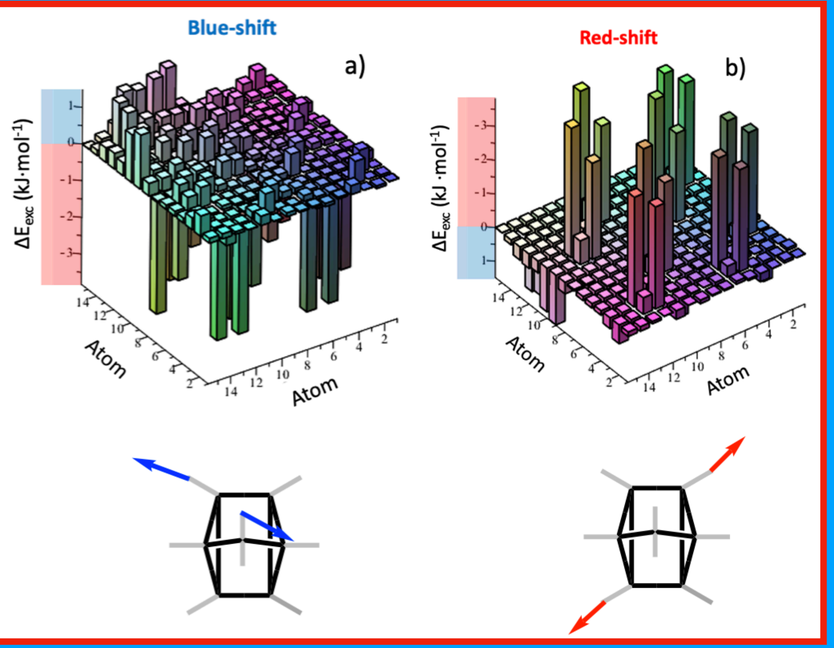




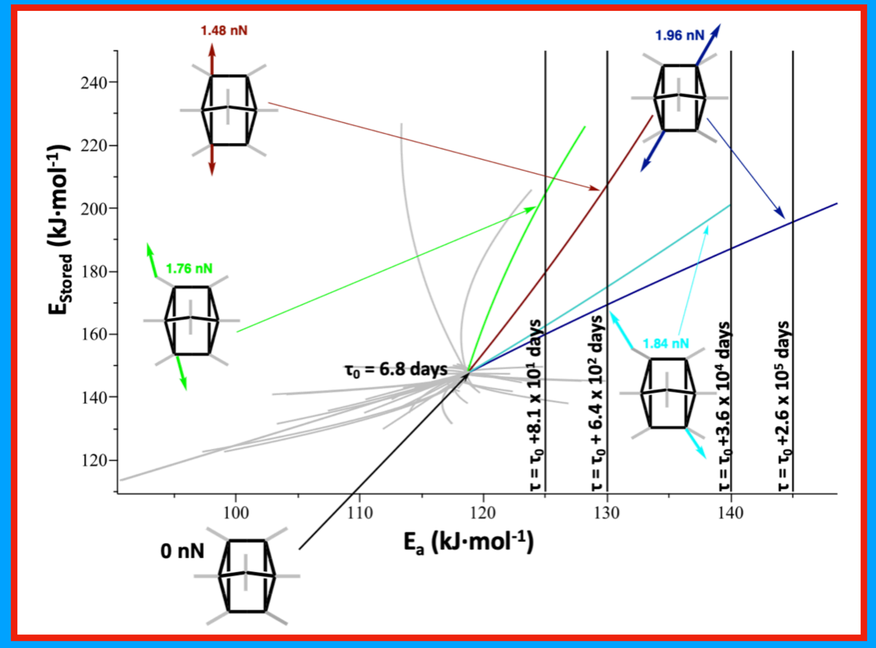
Mechanochemistry
Modulate the E_{exc}, E_a and $E_{estored}$



Force-Pair Induced Variation of the E_{exc}

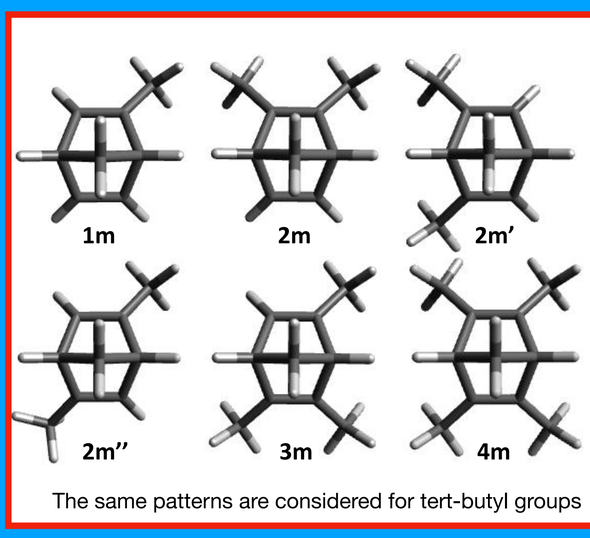


Force-Pair Induced Variation of E_a and Restored

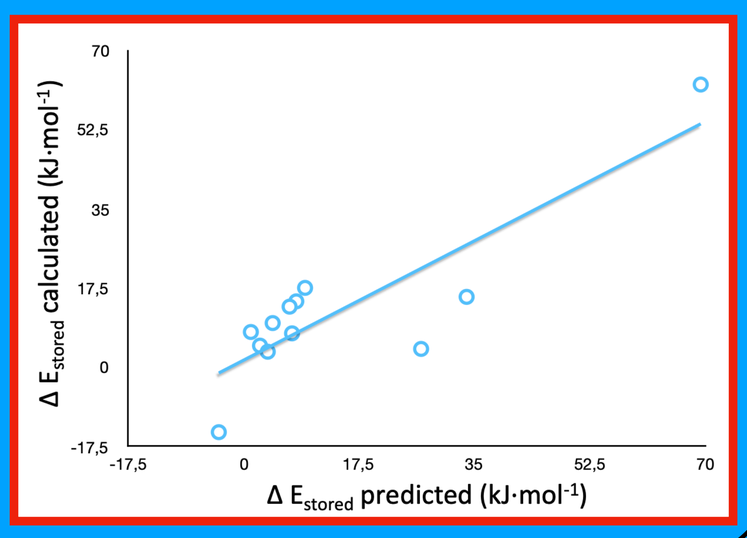


- ✗ The absorption energy cannot be significantly modulated (-3.5 kJ/mol red shift and +1 kJ/mol blue shift) → because of the chromophore nature
- ✓ Most of the forces have similar effects on E_{stored} and E_a. Only the forces acting on the four carbon/hydrogens atoms implied in the cyclization increase significantly both energies.
- ✓ The lifetime of the QC increase

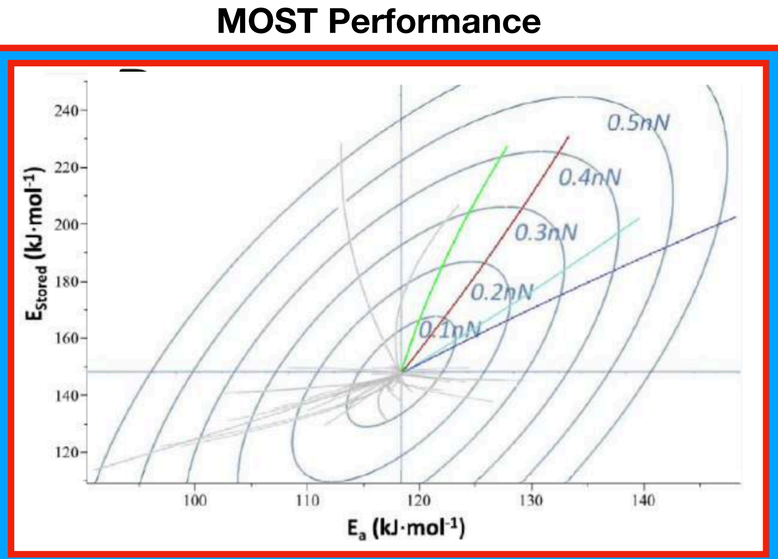
Substituent-Induced Mechanical Force



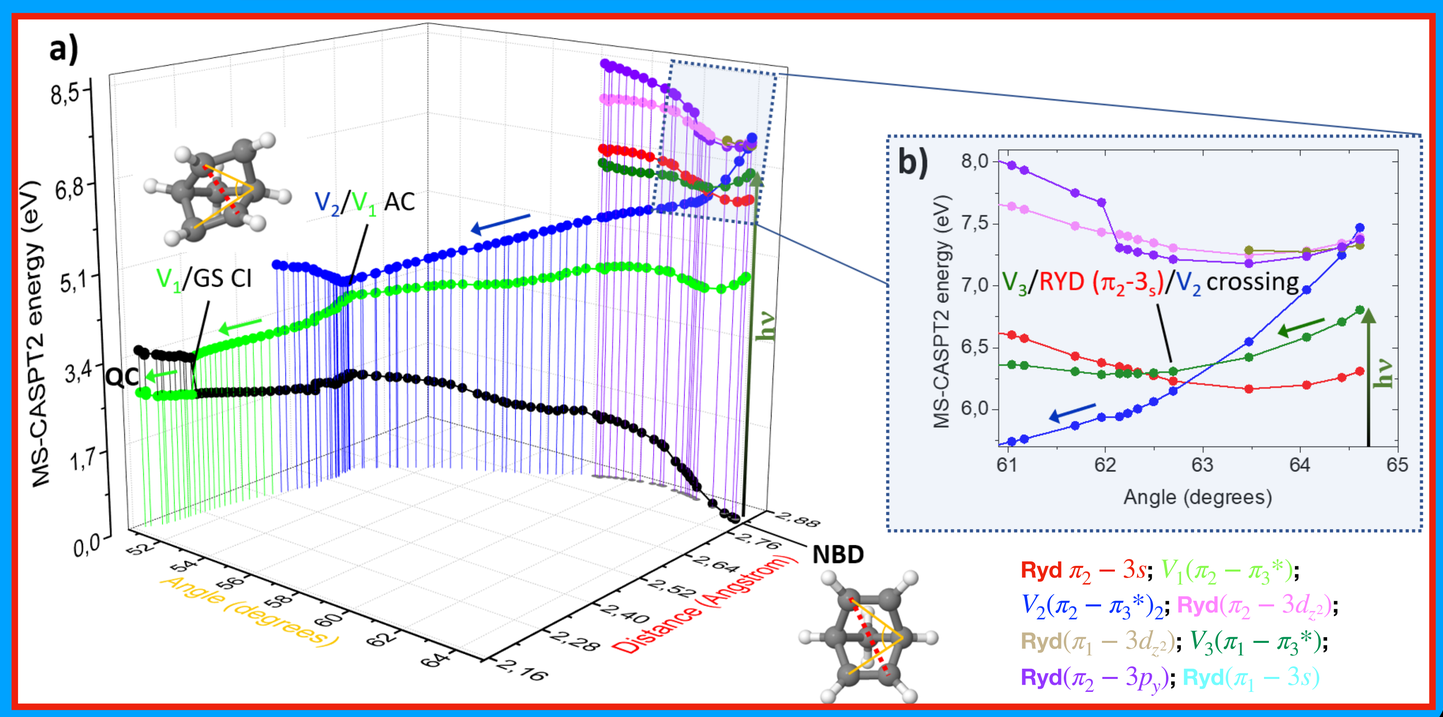
The same patterns are considered for tert-butyl groups



Mechanical Efficiency Limit for Improvement of MOST Performance



NBD→QC MS-CASPT2//CASSCF minimum energy path



Conclusion:

- It has been demonstrate that the norbornadiene/quadricyclane MOST system can be mechanochemically modulated and the application of external forces permits to significantly increase its performance.
- the effects of dynamic electronic correlation must be included to avoid a misleading description of the photochemical pathways.

References:

Mechanochemical Improvement of Norbornadiene-Based Molecular Solar-Thermal Systems Performance, Martina Nucci, Marco Marazzi, and Luis Manuel Frutos, ACS Sustainable Chemistry & Engineering 2019, 7 (24), 19496-19504

Acnowledgements:

This research was supported by the Spanish MINECO grant CTQ2016-80600-P and by the University of Alcalá (CCGP2017-EXP/027). M.N. is grateful to Spanish Ministerio de Ciencia, Innovacioán y Universidades, for a doctoral fellowship.