



Supramolecular Chemistry: Molecular Machines



The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2016 to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa "for the design and synthesis of molecular machines".

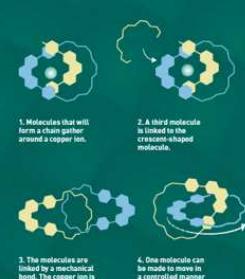
The Nobel Prize 2016 in Chemistry



They built the world's smallest machines

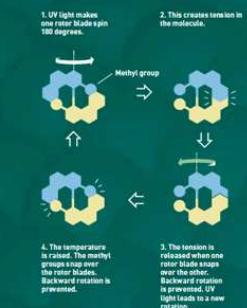
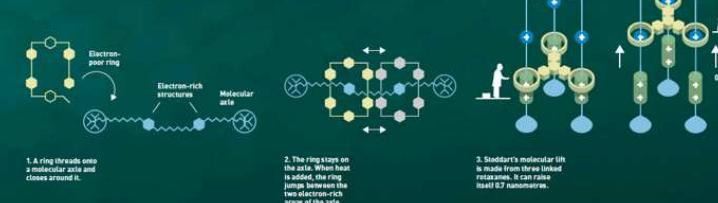
A tiny lift, artificial muscles and minuscule motors. The Nobel Prize in Chemistry 2016 is awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa for their design and production of molecular machines. They have developed molecules with controllable movements, which can perform a task when energy is added.

The development of computers demonstrate how the miniaturisation of technology can lead to a revolution. The 2016 Nobel Laureates in Chemistry have developed machines that are thousands of times smaller than a strand of hair. Normally all movements in chemical reactions are governed by chance. In the molecular machines that are now being created, movement is ordered and has a direction, which is necessary for them to be able to perform a task.



Sauvage moves chemistry away from chance
In order for a machine to perform a task, it must consist of parts that can move in relation to each other. Jean-Pierre Sauvage produced a molecule that fulfilled this requirement in 1983, when he linked two ring-shaped molecules together so that they could rotate around each other. Thanks to the chain's mechanical bond, the rings are free to move. In 1994, Sauvage succeeded in making one ring rotate around the other in a controlled manner.

In terms of development, the molecular motor is at the same stage as the electric motor was in the 1830s. Scientists then displayed various spinning cranks and wheels without knowing that they were the precursors of washing machines, fans and food processors. Molecular machines will probably be used in things such as new materials, sensors and energy storage systems.



Jean-Pierre Sauvage
Born 1939 in Paris, France. Professor Emeritus at the University of Strasbourg and Director of Research Emeritus at the National Center for Scientific Research (CNRS), France.

Sir J. Fraser Stoddart
Born 1942 in Edinburgh, UK. Board of Trustees Professor of Chemistry at Northwestern University, Evanston, IL, USA.

Bernard L. Feringa
Born 1951 in Barger-Compascuum, the Netherlands. Professor in Organic Chemistry at the University of Groningen, the Netherlands.

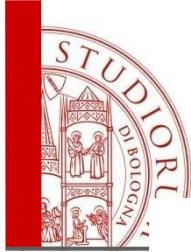


FURTHER READING More information on the Nobel Prize in Chemistry 2016: www.nobelprize.org. ARTICLES: • Capoccia, A. N. (2007). From Acid Rocker to the City of Angels, and all the Meccano in Between: A Glance into the Life and Mind of Sir Fraser Stoddart. *The GCUA USJ*, 26, 1–2. • Stoddart, J. F. (2008). The Matter of Chemical Topology. *Chem Soc Rev*, 37, 1621–1629. • Weber, L., & Feringa, B. L. (2009). We Must be Able to Shape How Science is Done. *Nature Chem.*, 4(8), 102–104. • Feringa, B. L. (2010). The Twisted Logic: A tale of molecular rotors, rotaxanes, switches and pumps. *Nature*, 465, 18–21. VIDEOS: • Northwestern (2008, May 26). *Nanotechnology Town Hall Meeting - Sir J. Fraser Stoddart*. <https://www.youtube.com/watch?v=OzR8hDfZqg>. • Francis Wilford (2011, Nov. 16). A four-wheel molecular motor moving on a metal surface. <https://www.youtube.com/watch?v=6Spjy5C5c>. • Elsevier Journals (2016, Sept. 7). *Retirement Photo 2016*. <https://www.youtube.com/watch?v=tF-AHnCzCtA>. • International Institute for Nanotechnology at Northwestern University (2016, Oct. 10). *Nobel Laureate, Sir Fraser Stoddart, Speaking at 2016 IIN Symposium*. https://www.youtube.com/watch?v=qHfPvIuL_9.

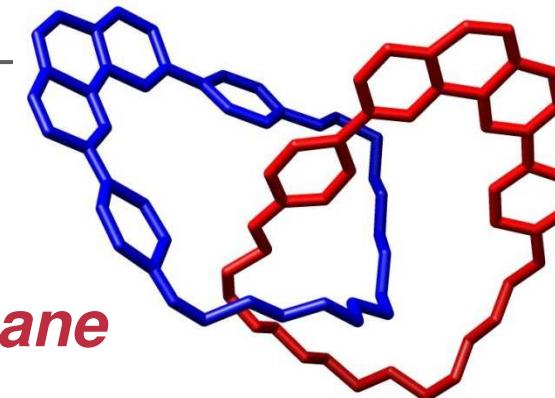
Editor: Gunilla von Heijne, Chief Executive and Sara Skoglund, Line
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The Royal Swedish Academy of Sciences. Graphic design: Stefan
Illustrations: Antoni Corrao/Corrao Graphics on PhotoAlto.

Printers and
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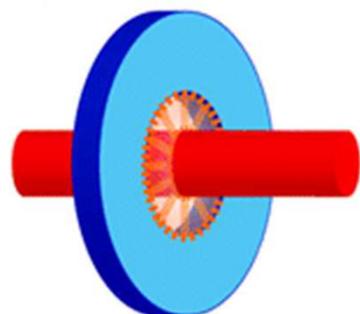


Mechanically-interlocked architectures

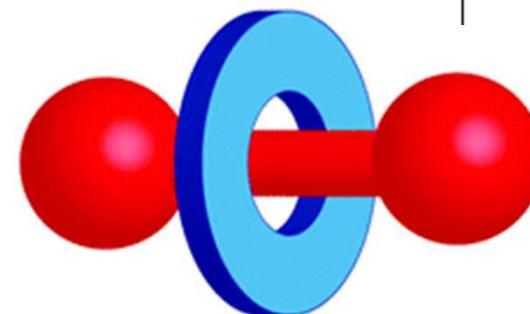


Catenane

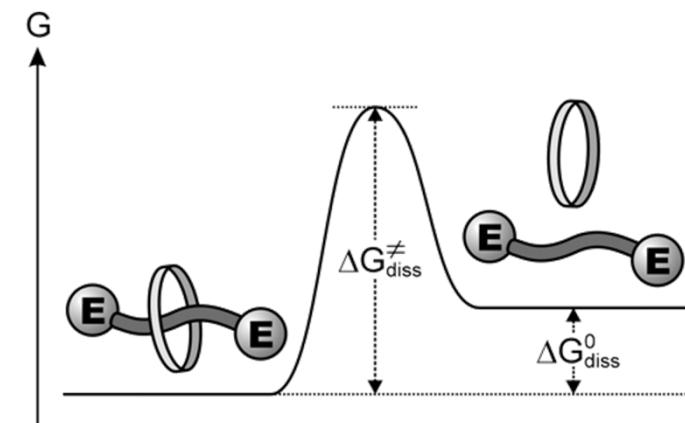
Pseudorotaxane

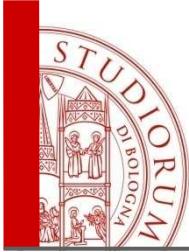


addition of
bulky groups
→
(stoppering)

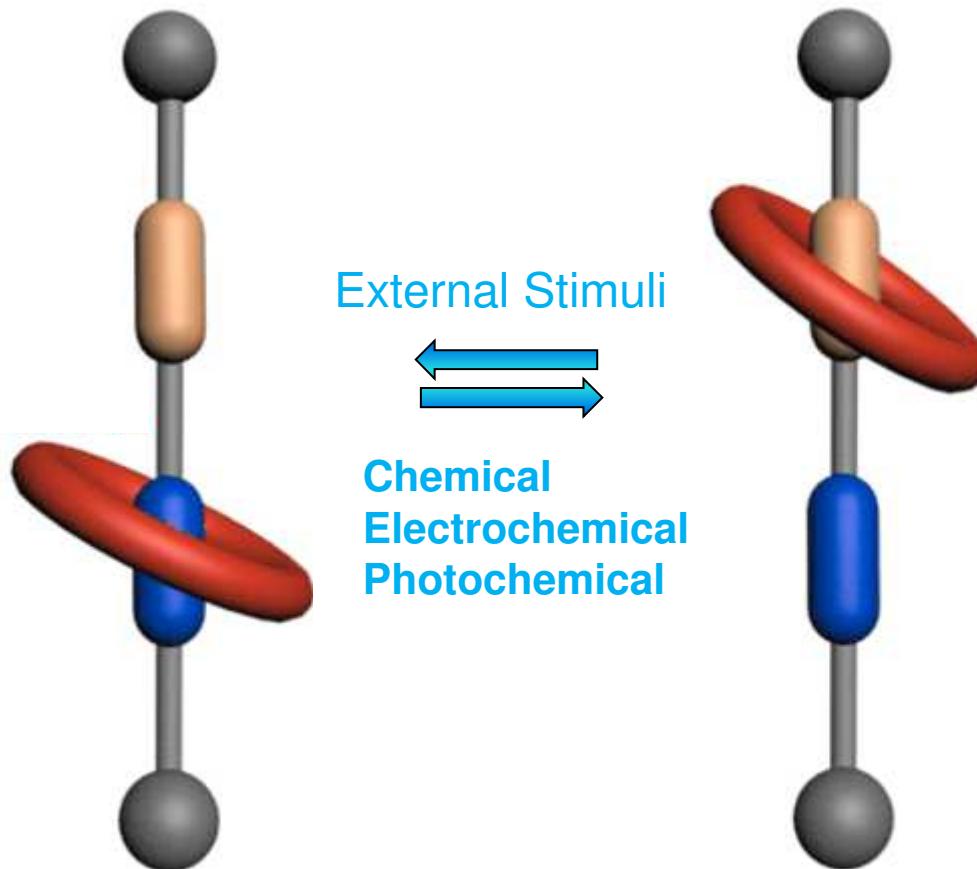


Rotaxane

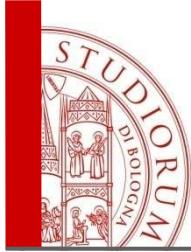




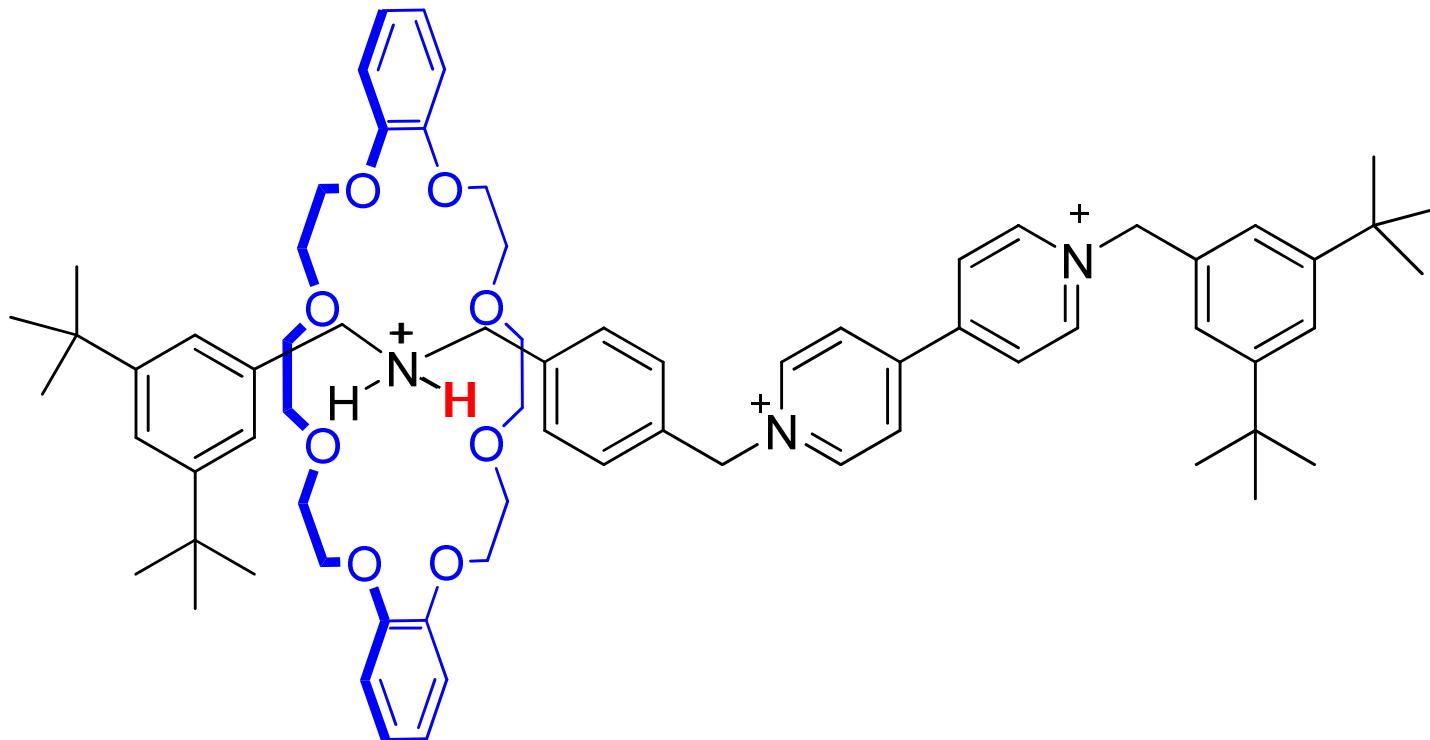
Will MIMs ever be of any practical use?



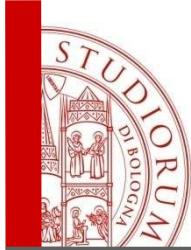
Switches and Logic Gates



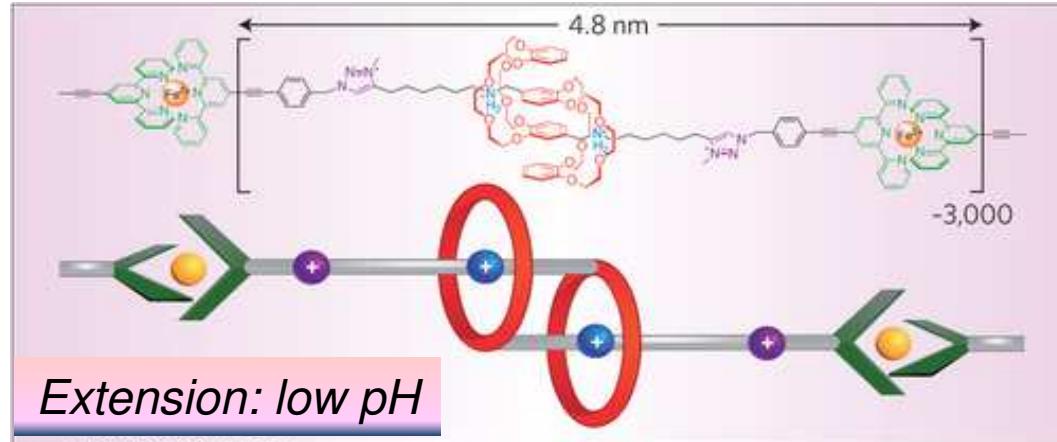
An acid-base controllable molecular shuttle



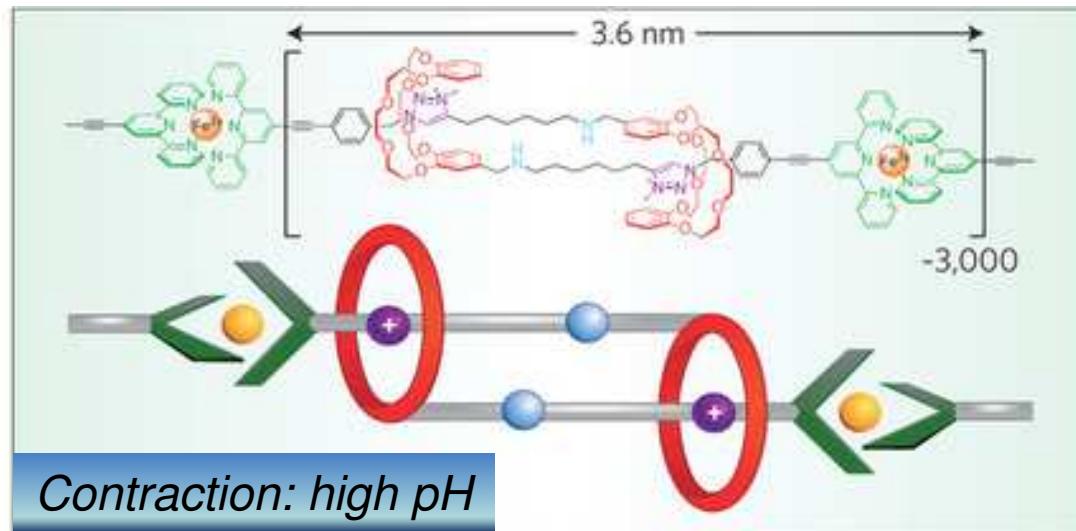
V. Balzani, J. F. Stoddart et al. JACS, 1998, 120, 11932

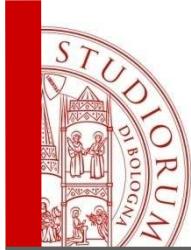


Will MIMs ever be of any practical use?

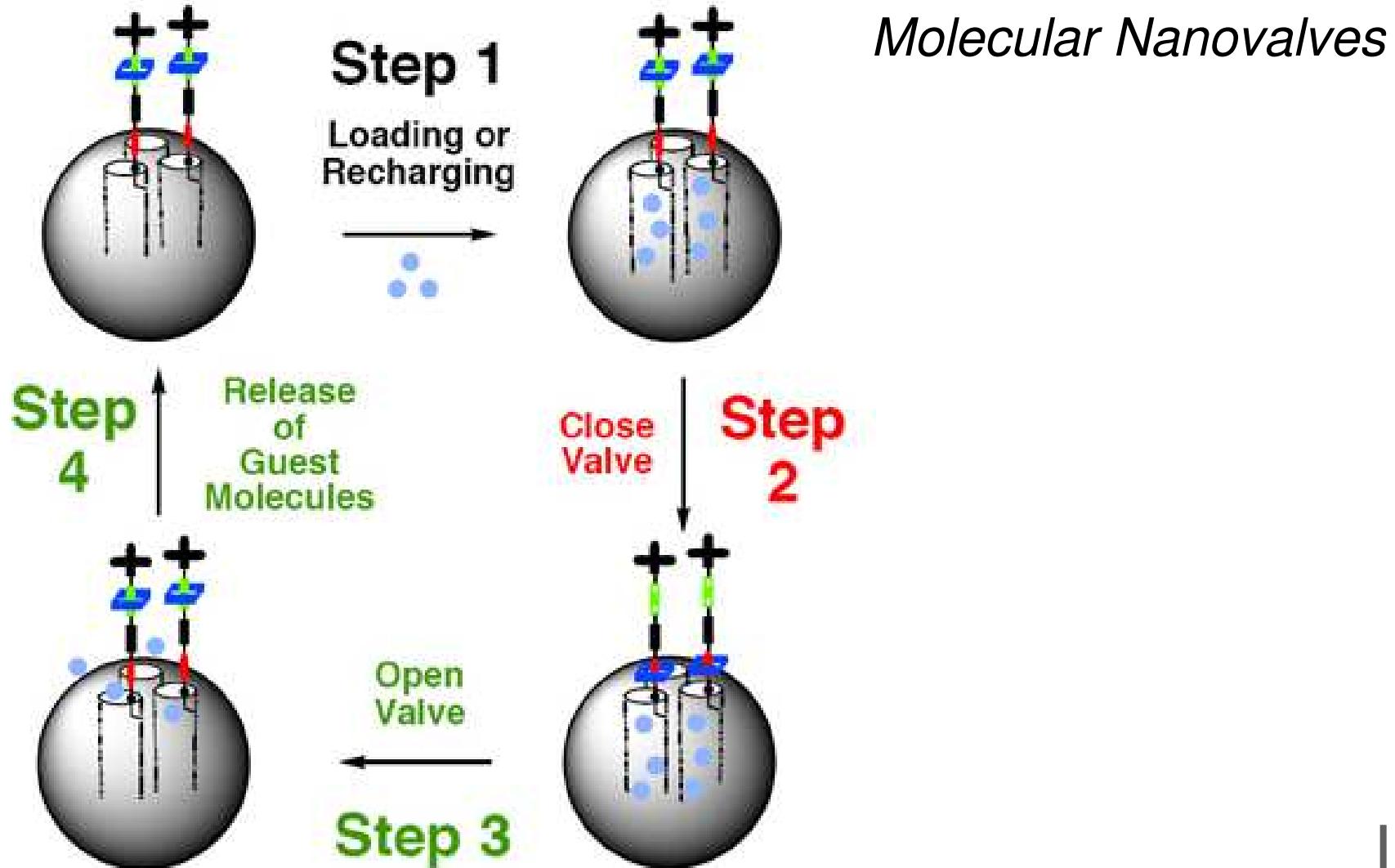


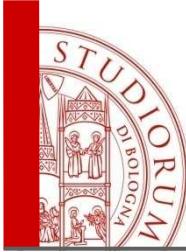
Artificial Muscles





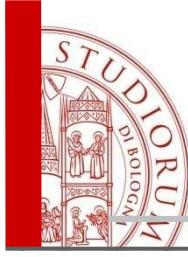
Will MIMs ever be of any practical use?





EPR (Risonanza di spin elettronico) Il cugino povero della RMN!





Why EPR ?

10^6 10^3 10^0 10^{-3} 10^{-6} 10^{-9} 10^{-12} 10^{-15} Time / s

Stopped Flow

NMR

EPR

Fluorescence

ps, fs Laserpulse

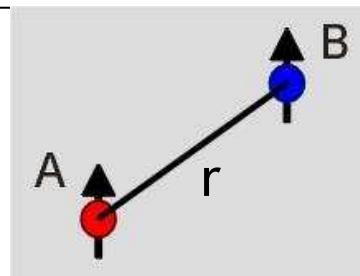


Faster time scale !

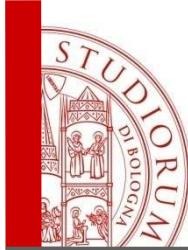
Classical range

Range of chemical kinetics

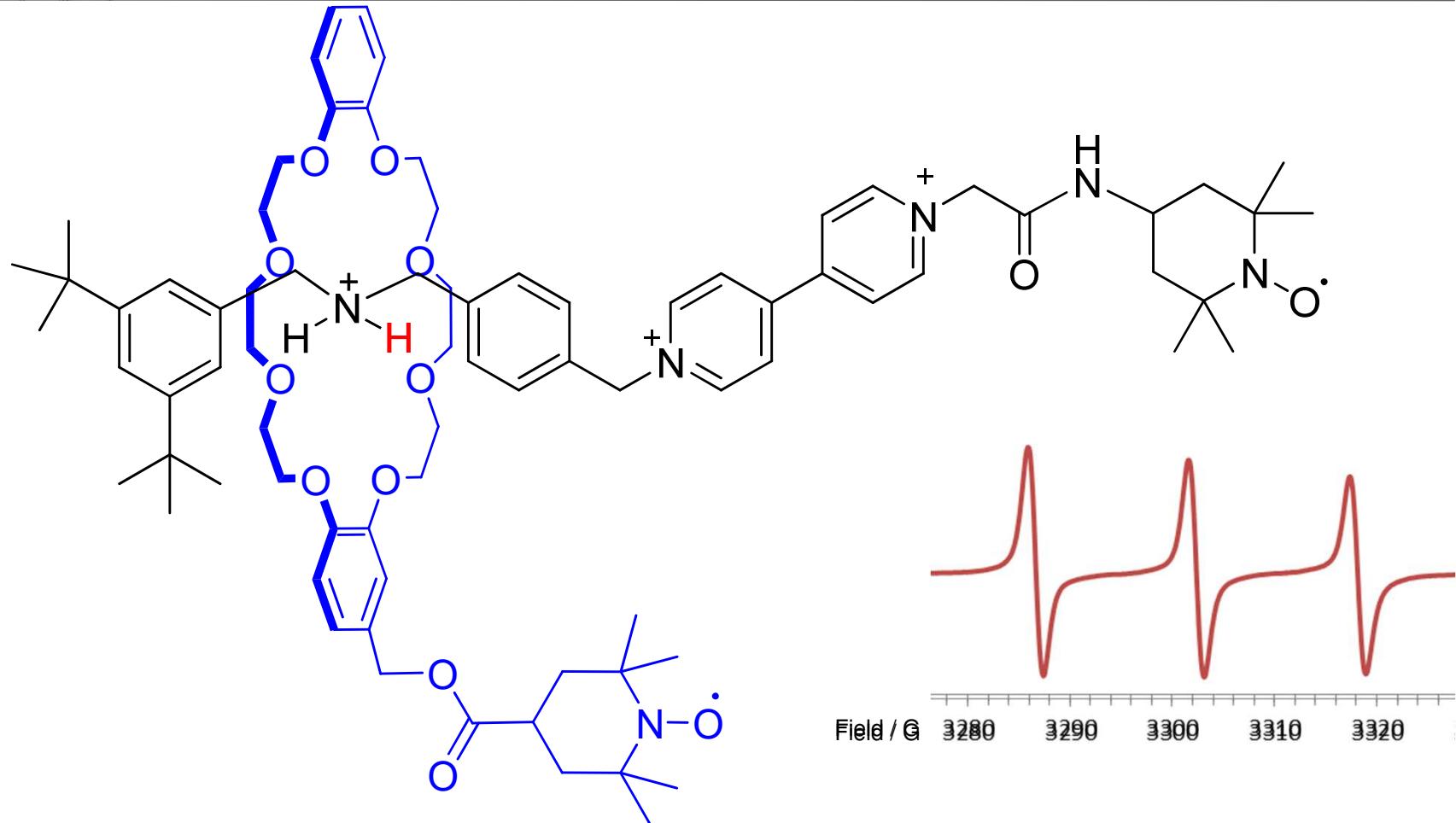
Spectroscopic range

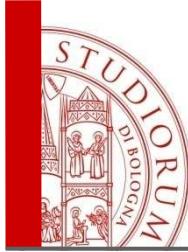


By EPR it is possible to obtain structural information at the nanometer scale

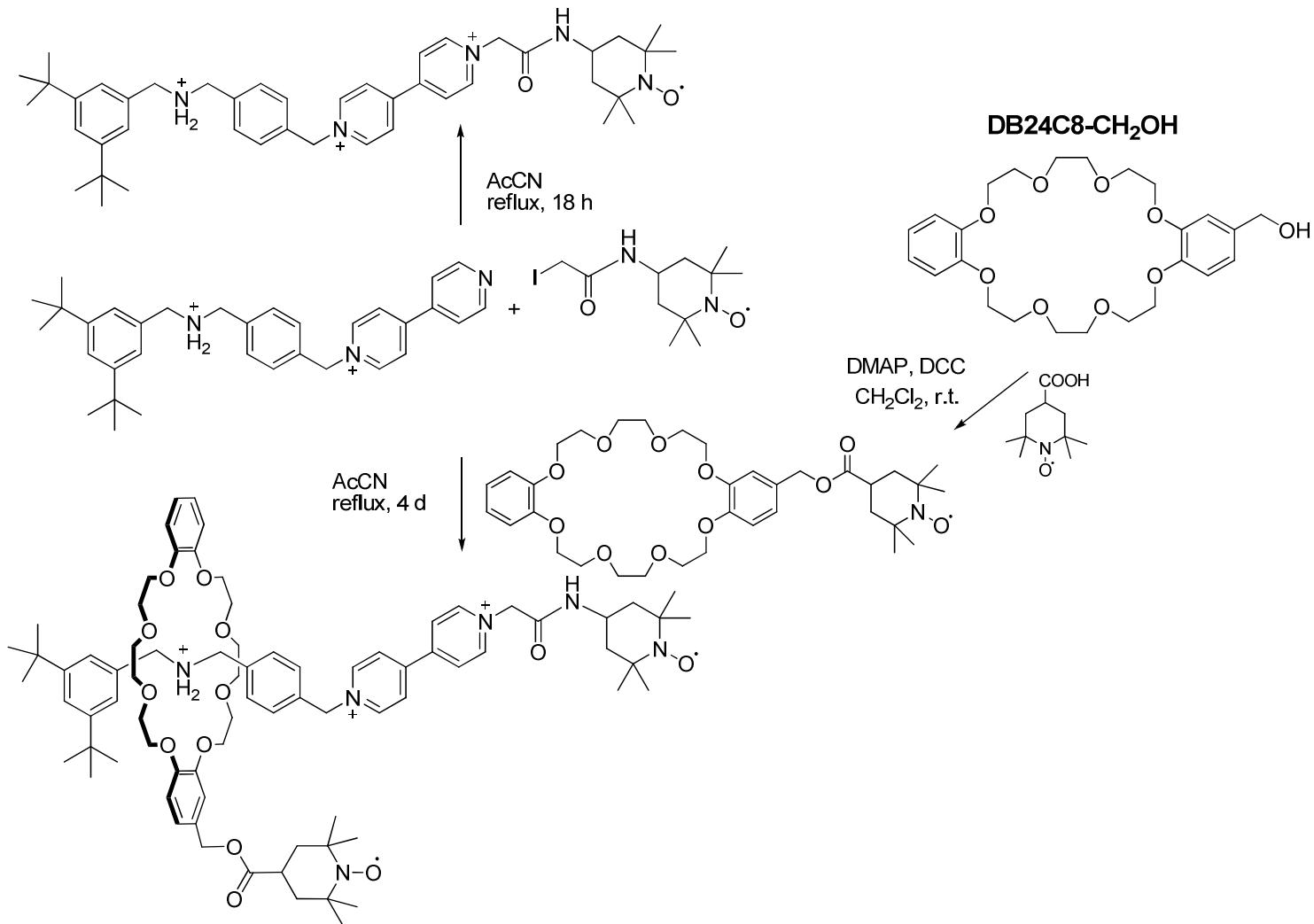


Probing the movement by EPR

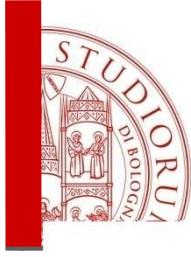




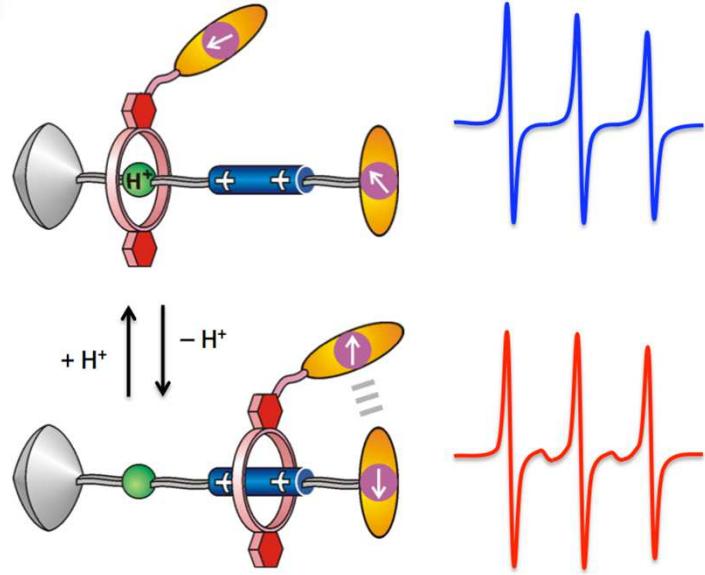
A novel spin labeled macrocycle

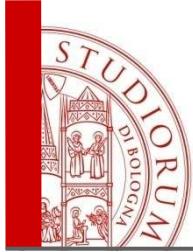


Valentina Bleve



Una macchina molecolare che trasporta «spin»

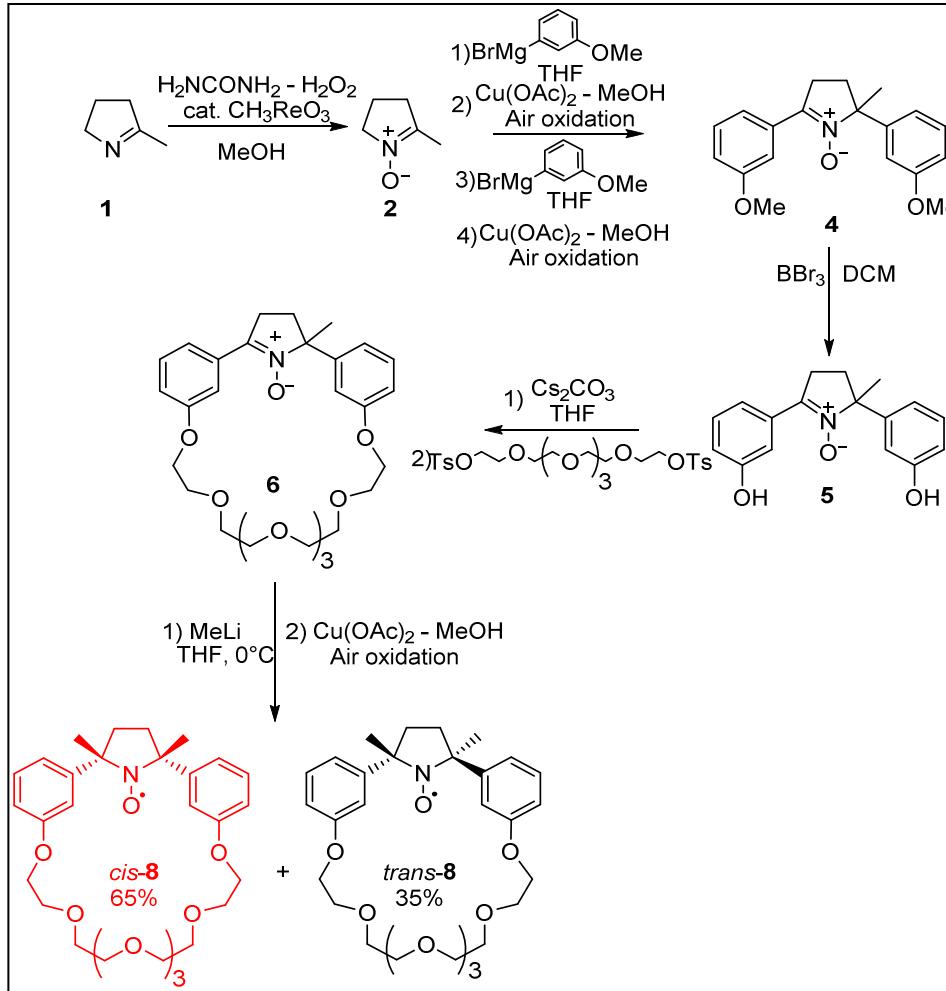


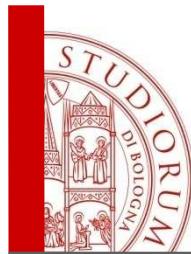


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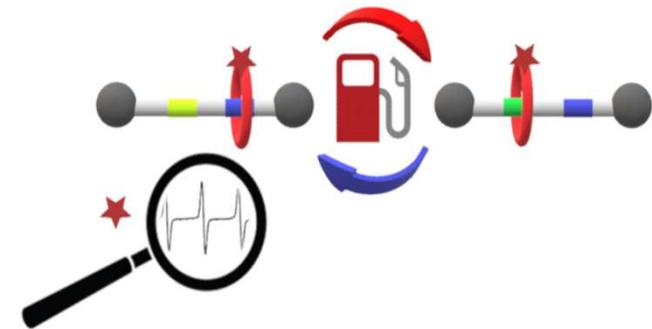


Cecilia
Poderi

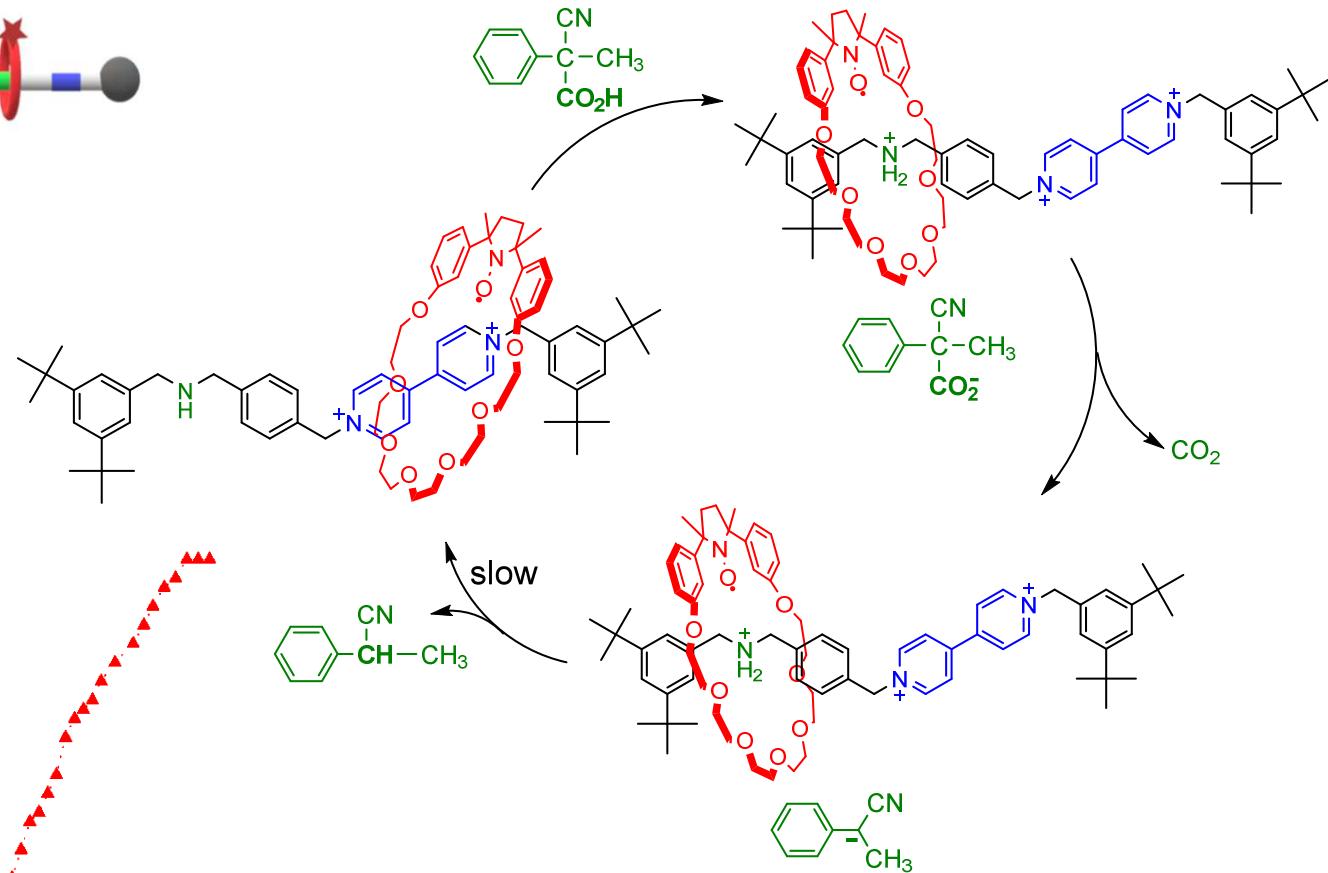
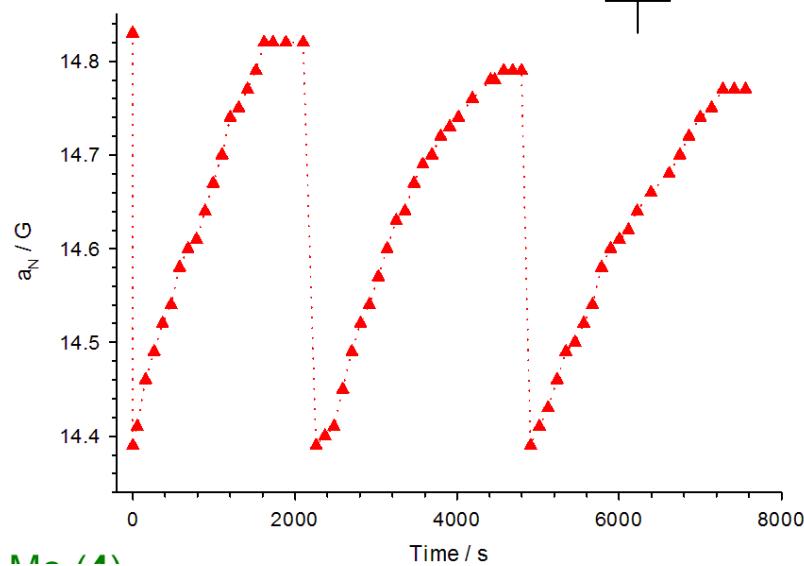


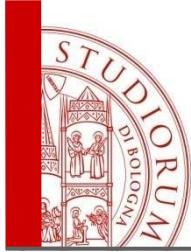


Back and forth switching motions monitored by EPR



J. Org. Chem., 2019, 84, 9364

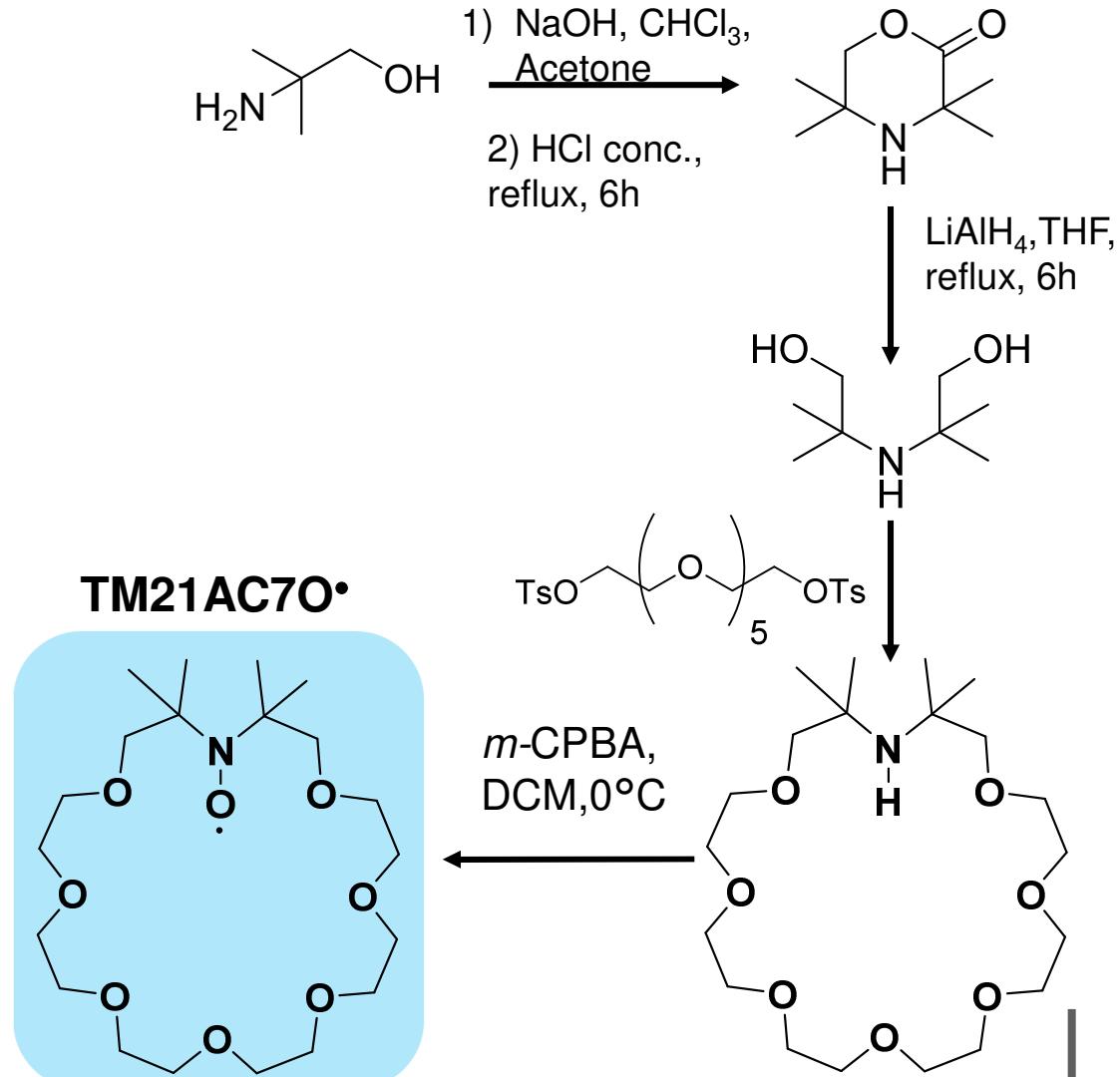


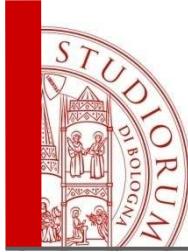


Improving EPR discrimination....

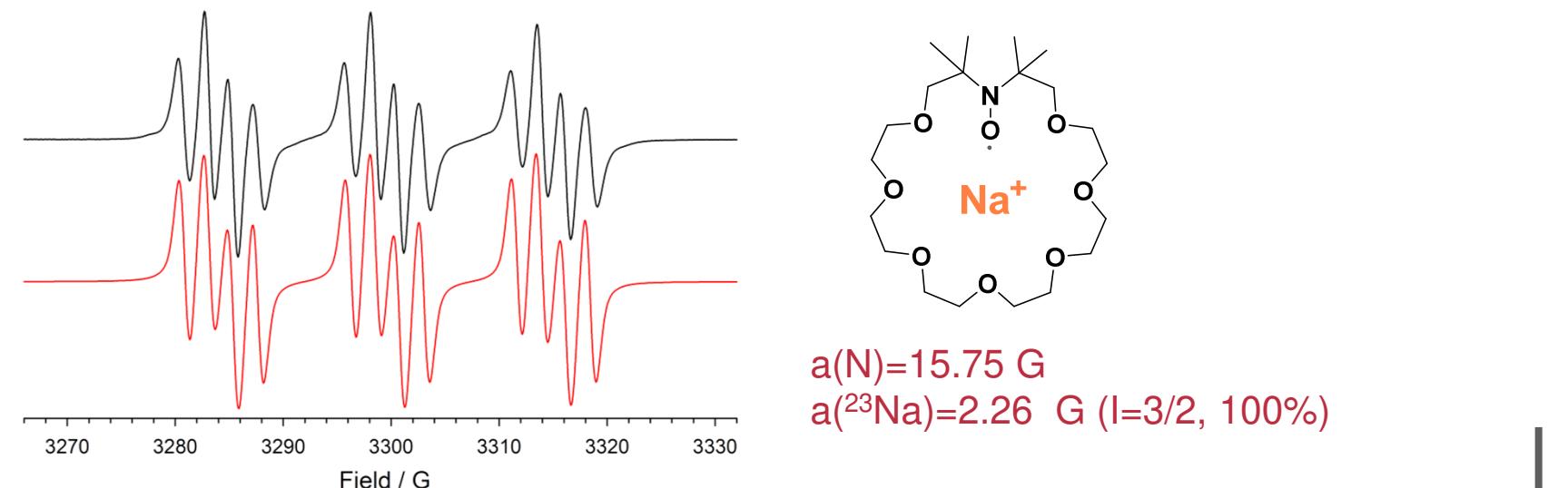
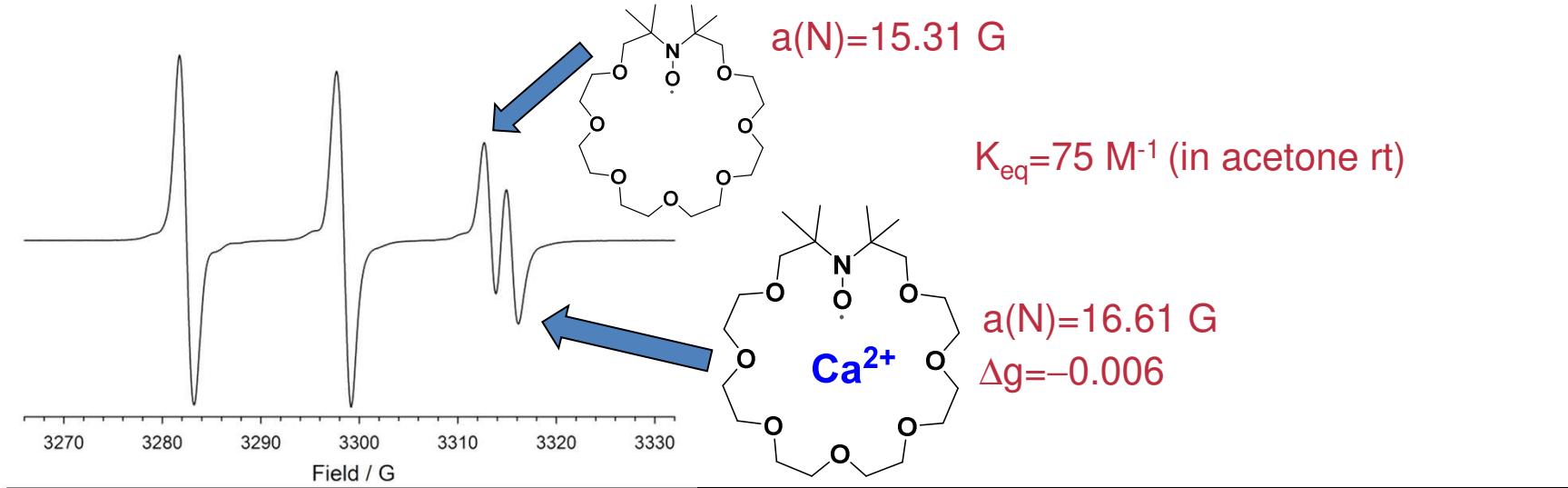


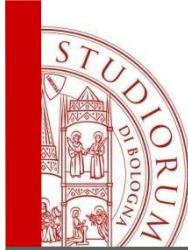
Iago
Neira





EPR discrimination of metal cations

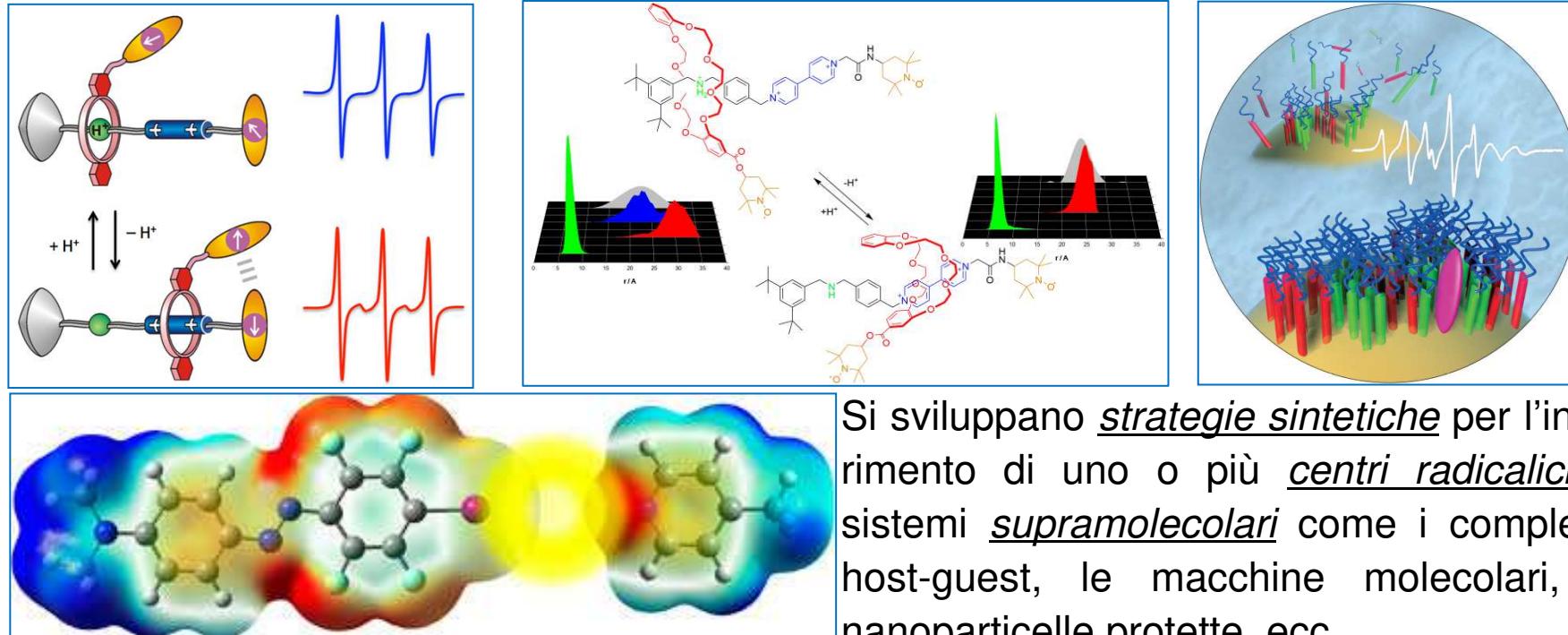




Sistemi supramolecolari paramagnetici

Prof. Marco Lucarini, Prof. ssa Elisabetta Mezzina, Dott. ssa Paola Franchi

Durata 6 mesi



La presenza di centri radicalici permette di studiare le strutture sintetizzate non solo con le tecniche tradizionali, 1D e 2D NMR, ESI-MS, spettroscopia UV, ma anche con la spettroscopia EPR (risonanza paramagnetica elettronica), tecnica in grado di fornire informazioni circa la dinamica di movimento, la forza delle interazioni e le distanze tra i vari componenti dell'assemblaggio molecolare.

(per informazioni dettagliate vedi *Eur. J. Org. Chem. 2020, 2995–3008*).