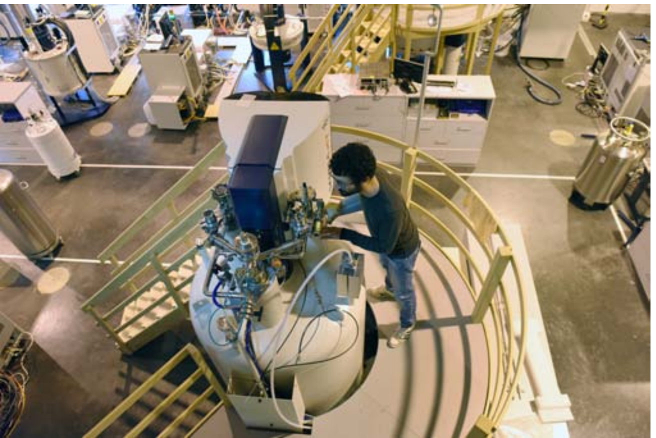
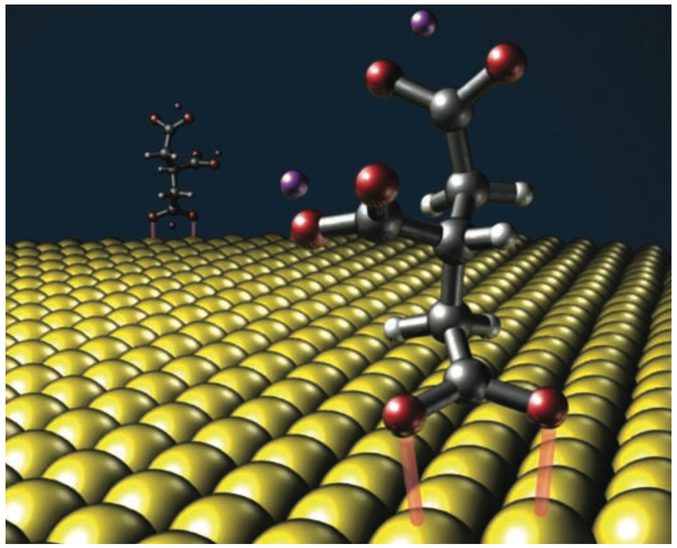
Hyperpolarized Solid-State NMR for Functional Materials

Anne Lesage

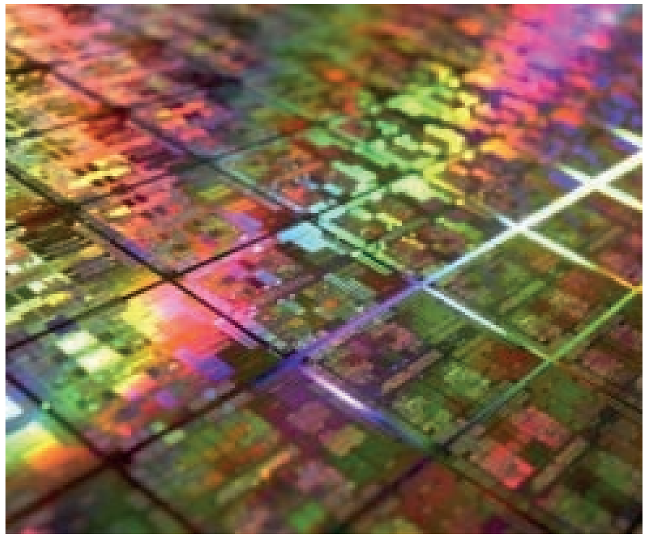
High-Field NMR Center of Lyon



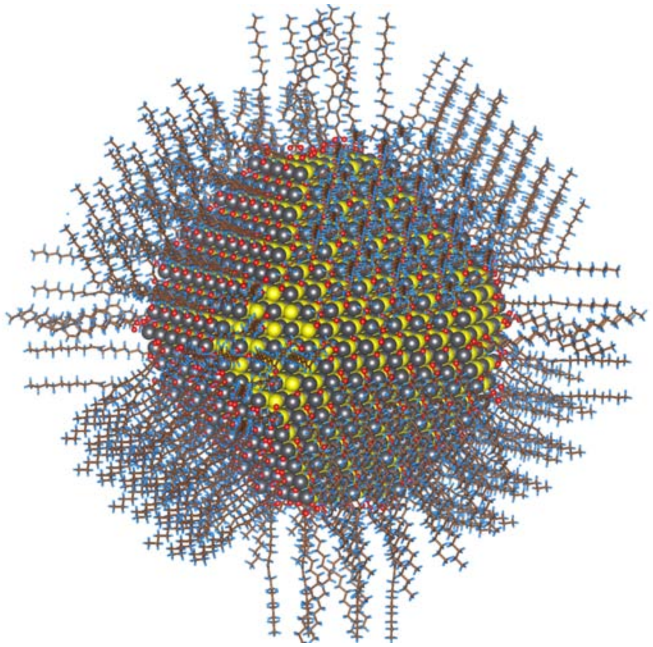
Functional Materials: Characterisation is the Key



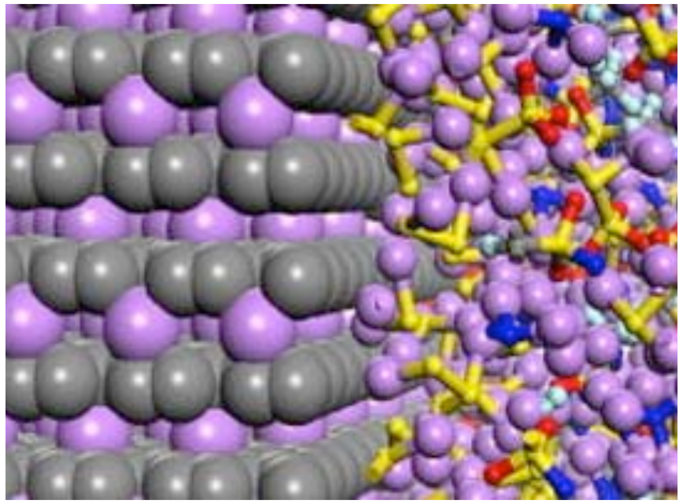
Surface organometallic catalysts



Wafers



Ligand-capped nanocrystals

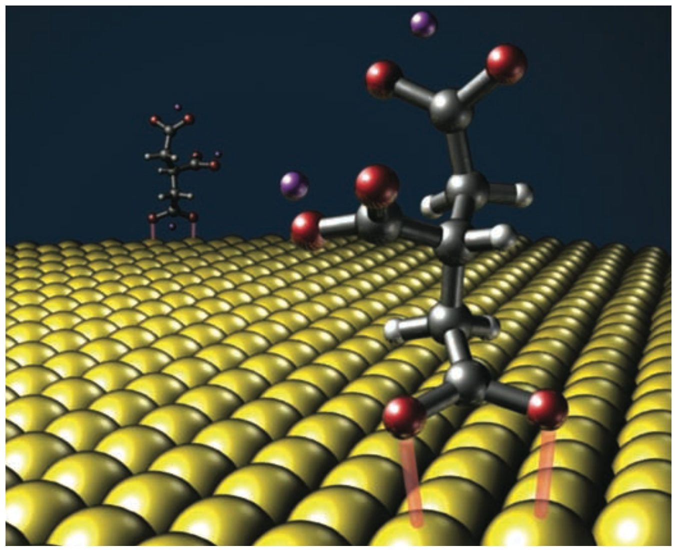


Battery materials

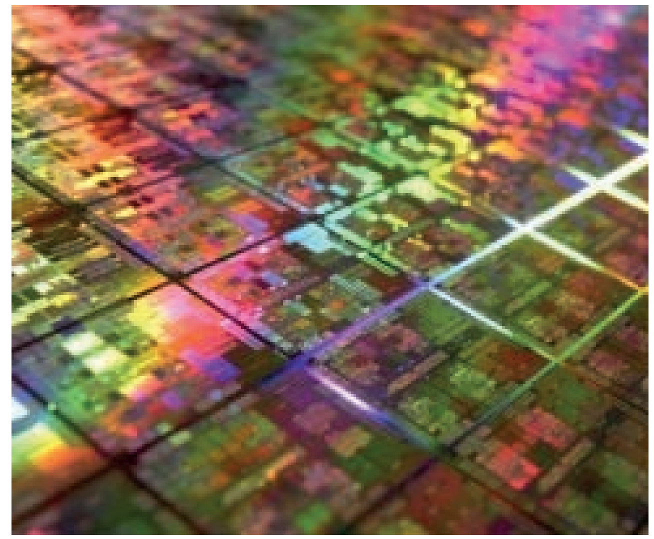
The properties of functional materials often result from their structure at surfaces or interfaces

Understanding these structures is essential to improve their performance

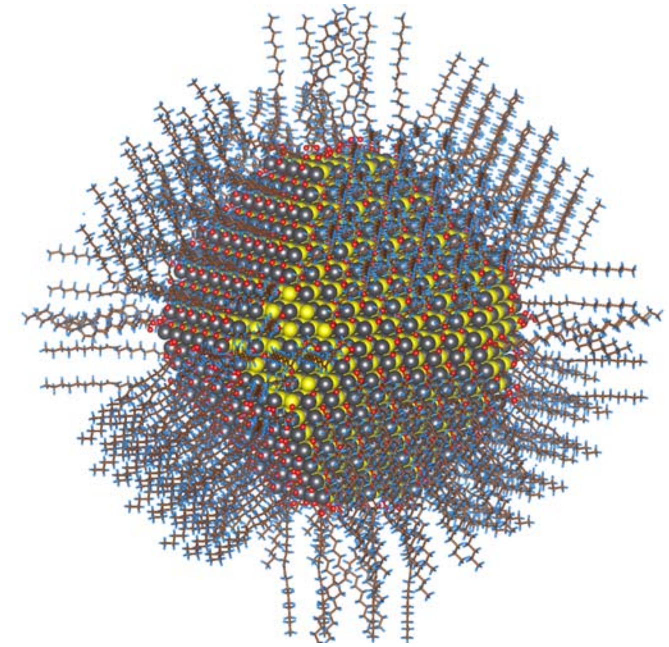
Functional Materials: Characterisation is the Key



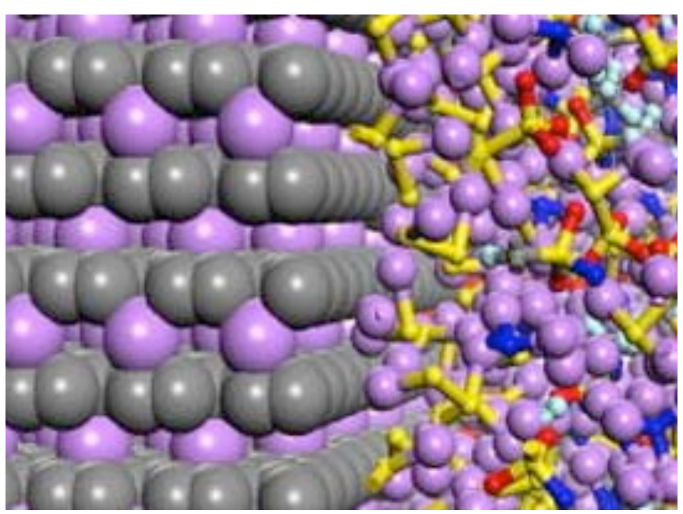
Surface organometallic catalysts



Wafers



Ligand-capped nanocrystals

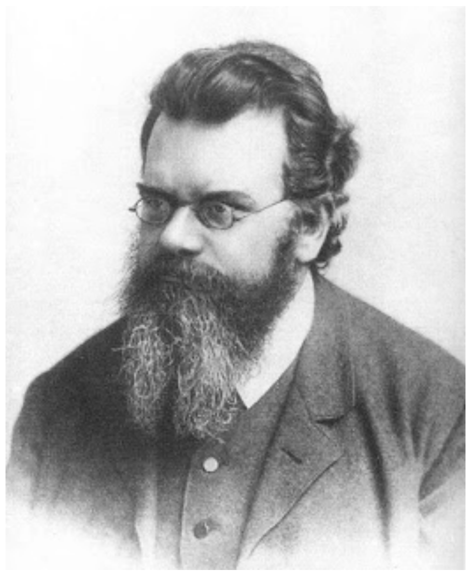


Battery materials

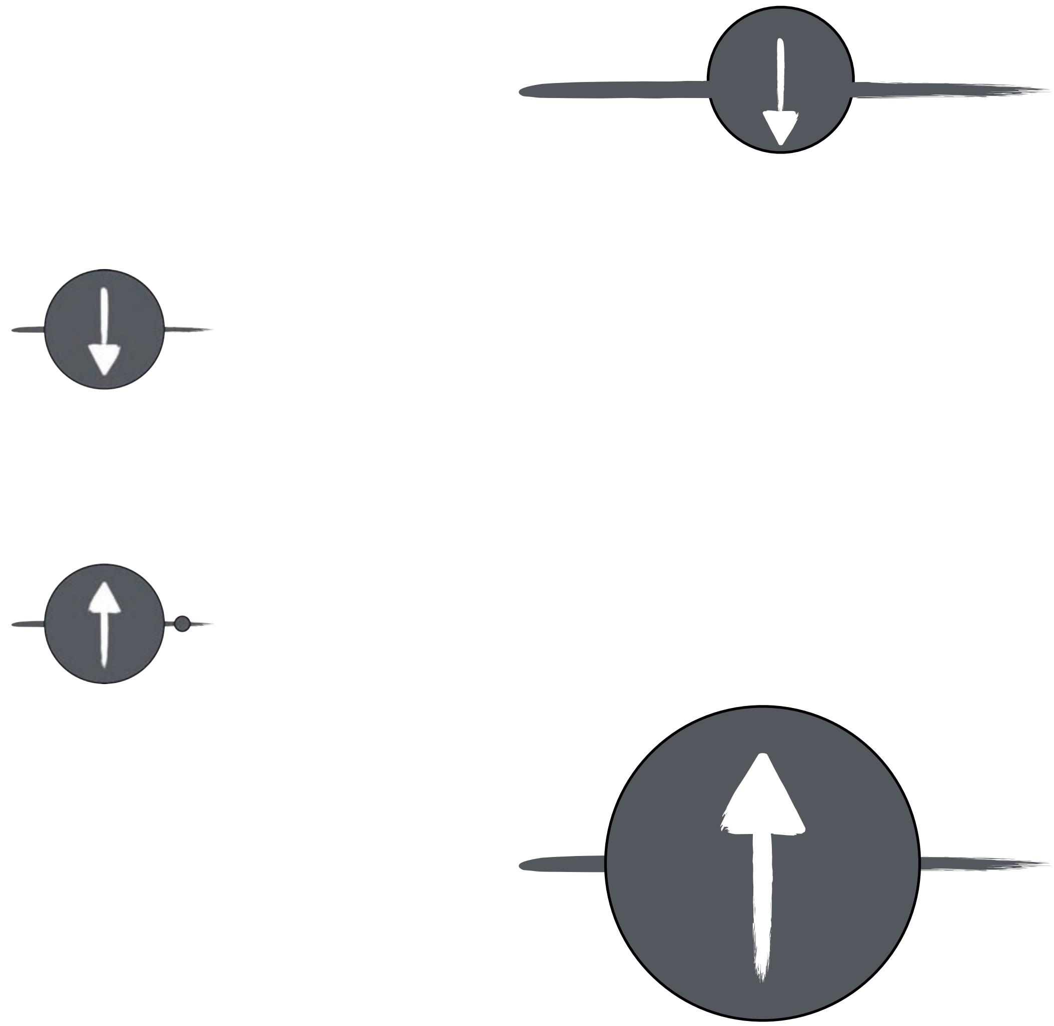
When surfaces can be characterised by NMR, information content is rich.

But the sensitivity is an issue and it requires high-surface area, high density of sites, isotopic labelling...

Why is NMR so insensitive?



Ludwig Boltzmann



$$\exp\left(\frac{-\hbar\omega}{k_B T}\right)$$

$$\gamma_{e^-} \approx 660 \cdot \gamma_{^1H} \approx 2650 \cdot \gamma_{^{13}C}$$

Unpaired electrons are much more polarized than nuclei !

Exploiting the electronic polarization

"Within the framework of the single particle model an enhanced nuclear polarization is predicted as the result of relaxation processes that occur when the electron-spin resonance is saturated."

Overhauser, October 1953

Charles P. Slichter
(1924- 2018)

First experimental evidence of successful electron polarization transfer to a 7Li nucleus by Carver and Slichter in 1953 !

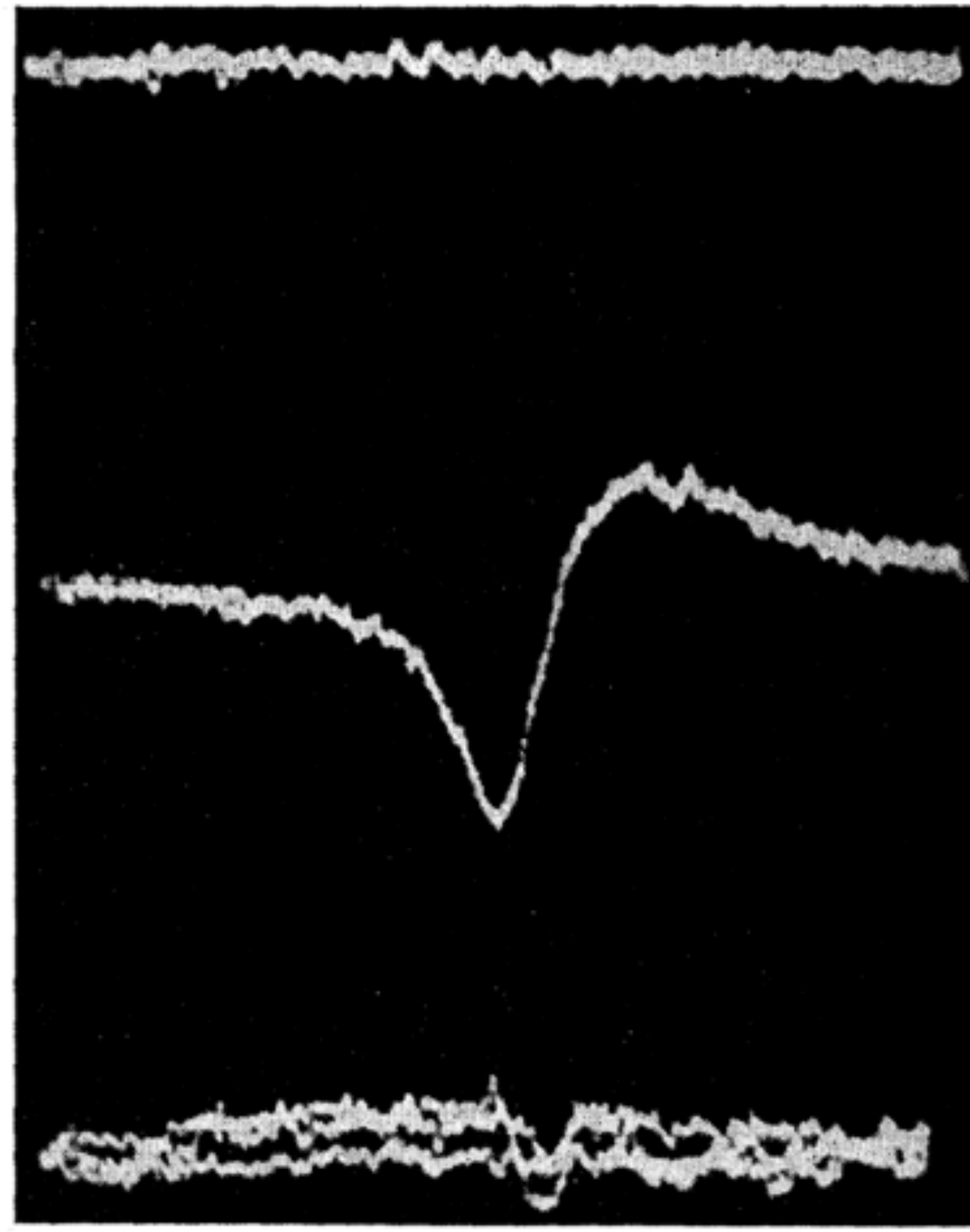
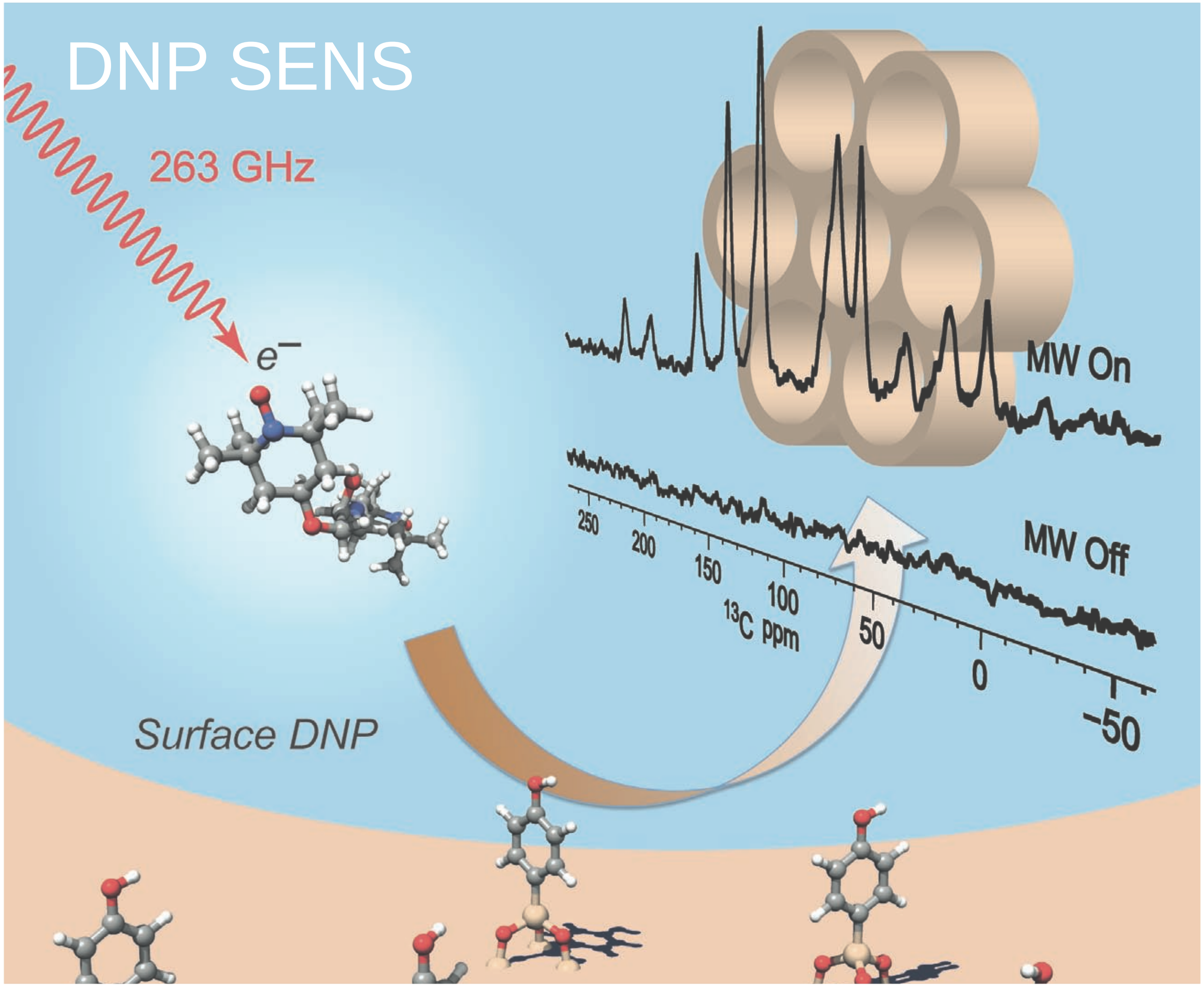


FIG. 1. Oscilloscope pictures of 50-kc/sec nuclear resonance absorption *vs* static magnetic field. Field excursion 0.2 gauss. Top line: Li^7 resonance (lost in noise). Middle line: Li^7 resonance enhanced by electron saturation. Bottom line: Proton resonance in glycerin sample.

« Dynamic Nuclear Polarization (DNP) »

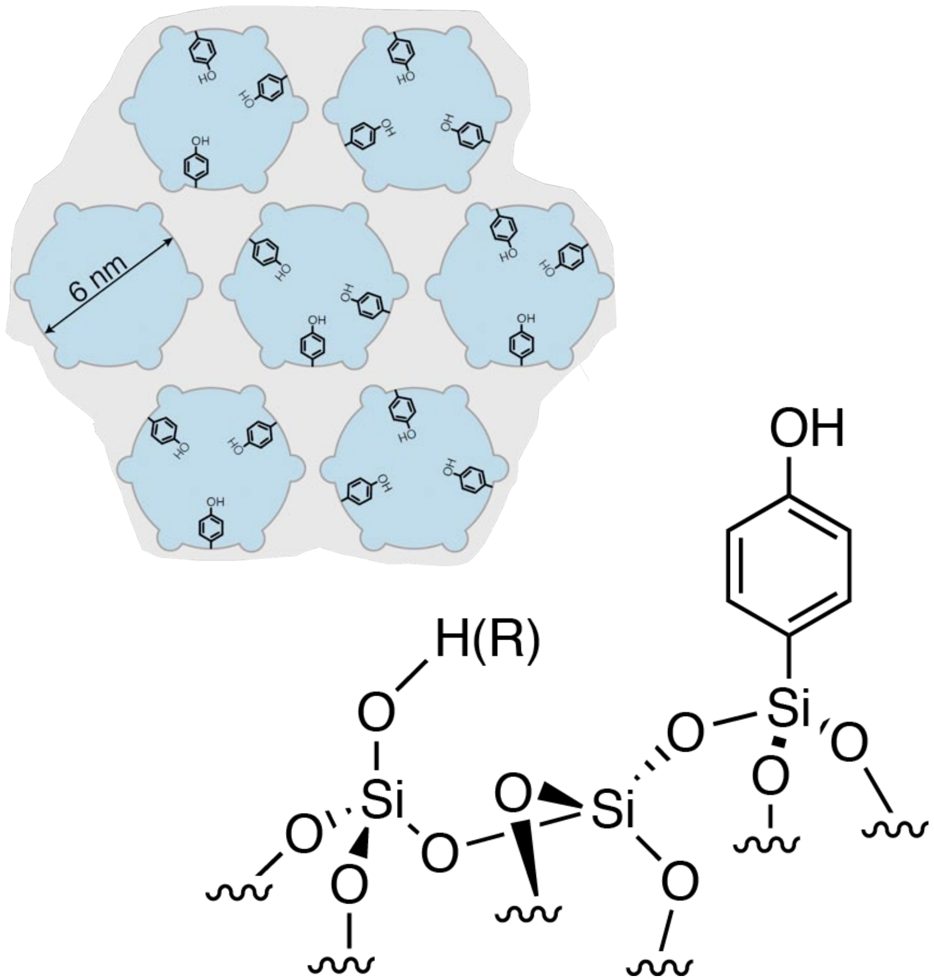
DNP Surface Enhanced NMR Spectroscopy: Touching the Surface



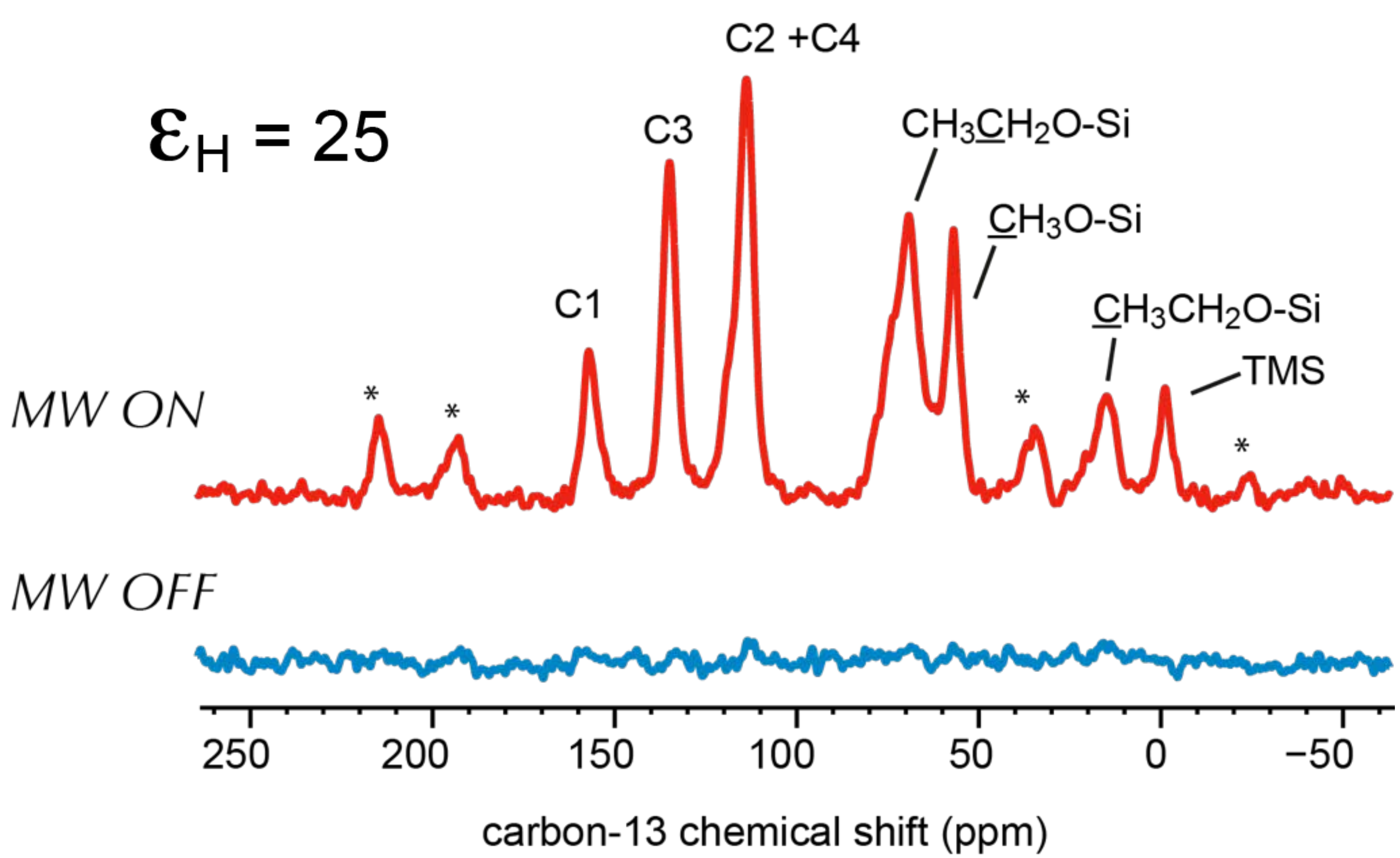
Ni, Q. Z. […] Temkin, R. J.; Herzfeld, J.; Griffin, R. G. « High Frequency Dynamic Nuclear Polarization ». *Acc. Chem. Res.* **2013**, 46 (9), 1933–1941.

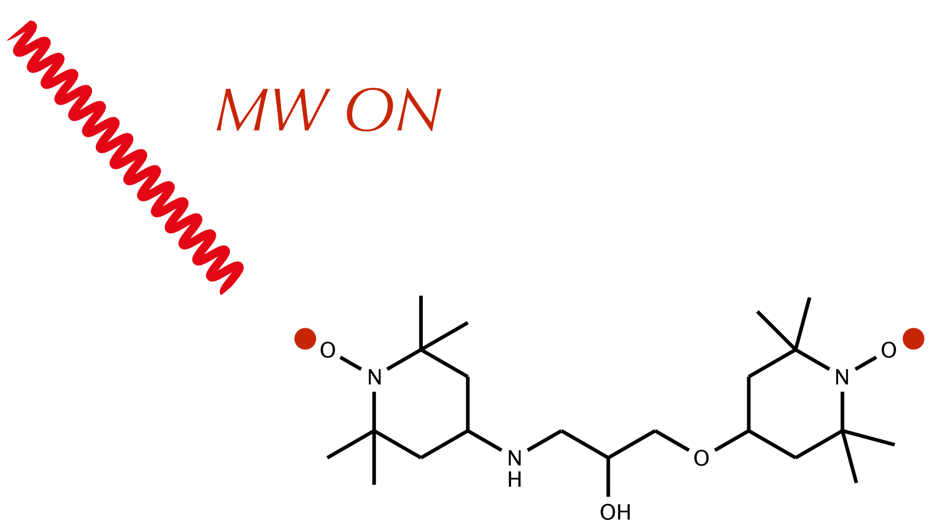
Rossini, A. J.; Zagdoun, A.; Lelli, M.; Lesage, A.; Copéret, C.; Emsley, L. » DNP Surface Enhanced NMR Spectroscopy. » *Acc. Chem. Res.* **2013**, 46 (9), 1942.
Berruyer, P.; Emsley, L.; Lesage, A. « DNP in Materials Science: Touching the Surface ». *eMagRes* **2018**, 7 (4), 93–104.

The Very First DNP SENS Experiments



Incipient wetness impregnation with
90:10 D_2O/H_2O & 25 mM TOTAPOL
T = 105 K, 263 GHz, 9.4 T, 10 kHz MAS

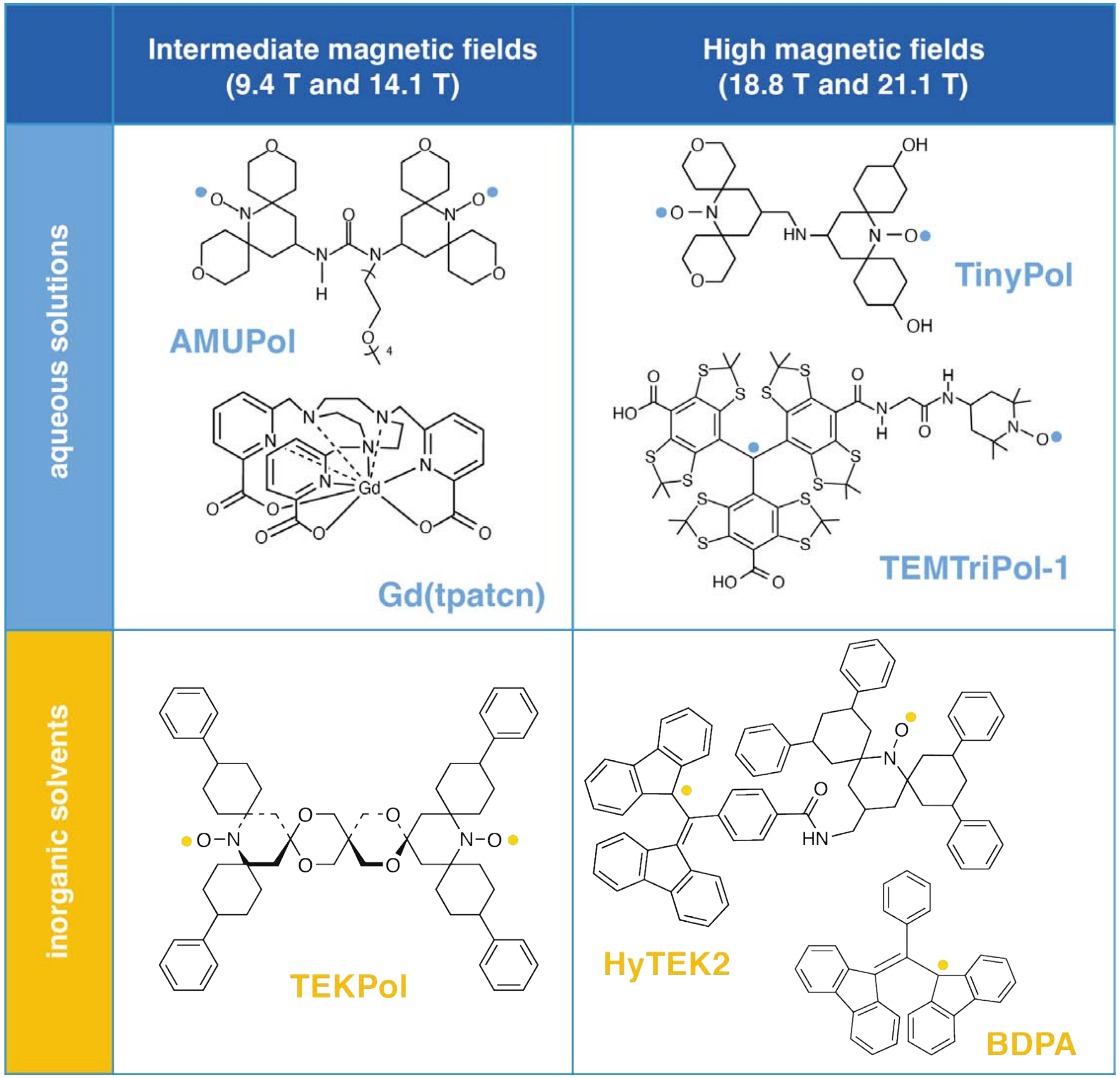


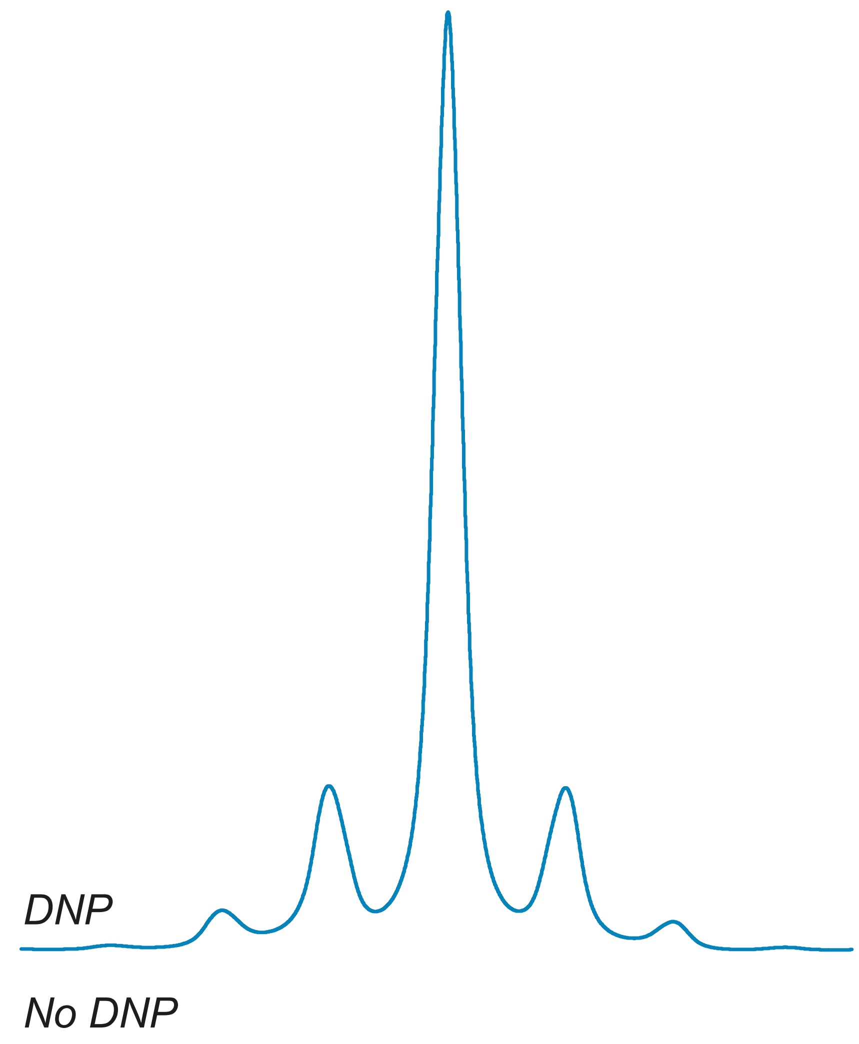


Lesage et al, *J. Am. Chem. Soc.* **132**, 15459 (2010)
Lelli et al, *J. Am. Chem. Soc.* **133**, 2104 (2011)

A Decade of Ongoing Fundamental Developments

A portofolio of polarising agents

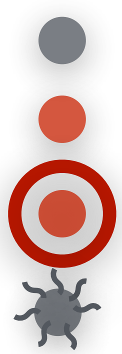




$\varepsilon_H > 200$ up to 21.1 T and 60 kHz MAS (at 100 K)

Casano, G.; Karoui, H.; Ouari, O. « Polarizing Agents: Evolution and Outlook in Free Radical Development for DNP ». *eMagRes* **2018**, 7, 195–208.

A Decade of Ongoing Fundamental Developments

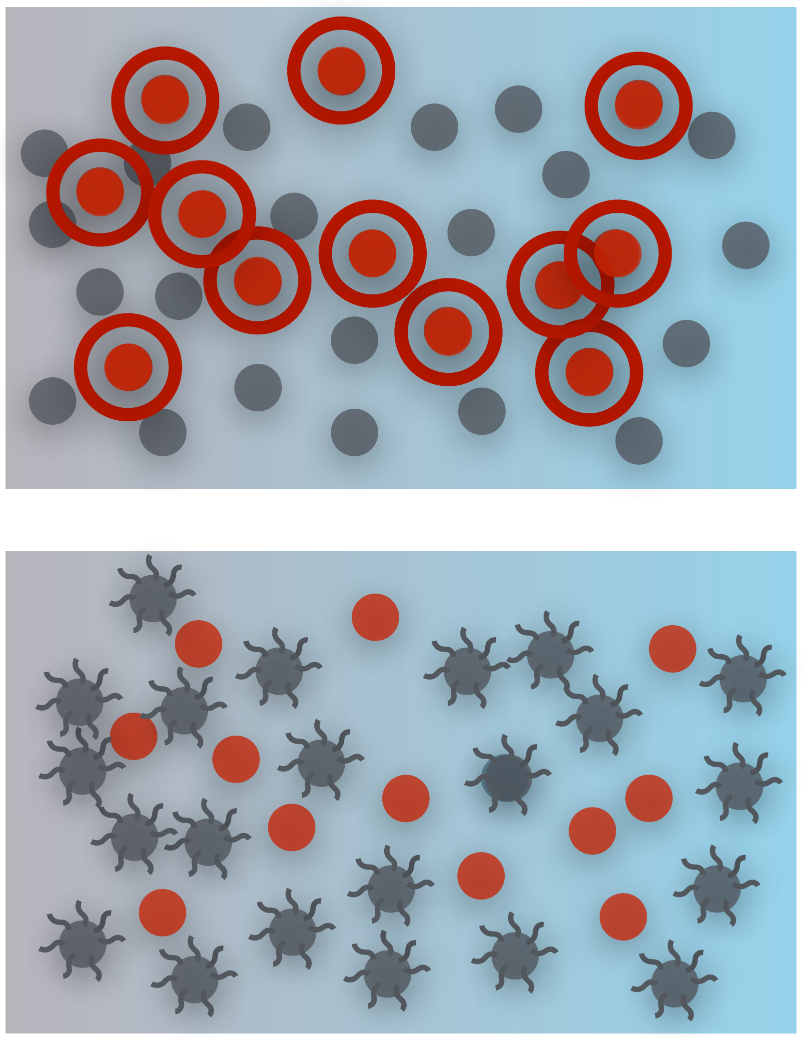


particles with reactive surfaces

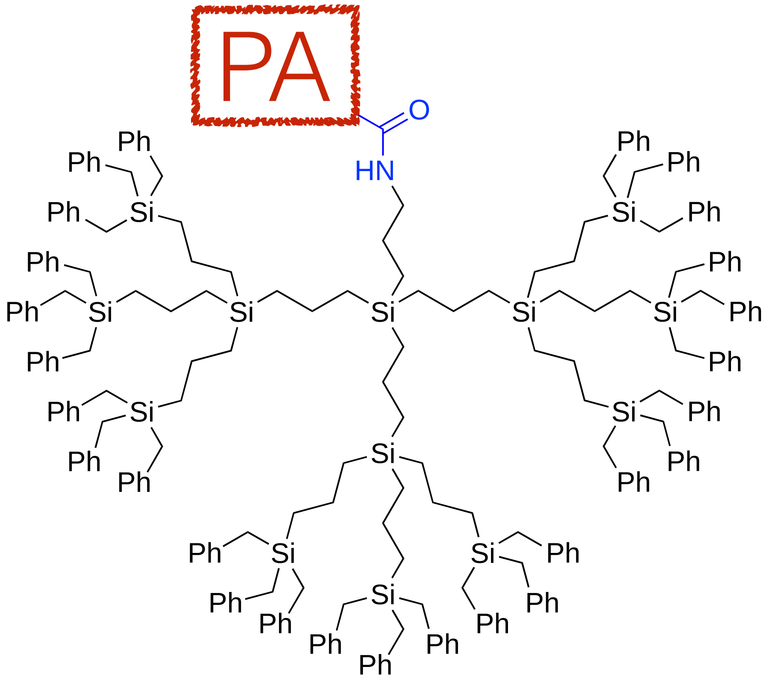
polarising agent

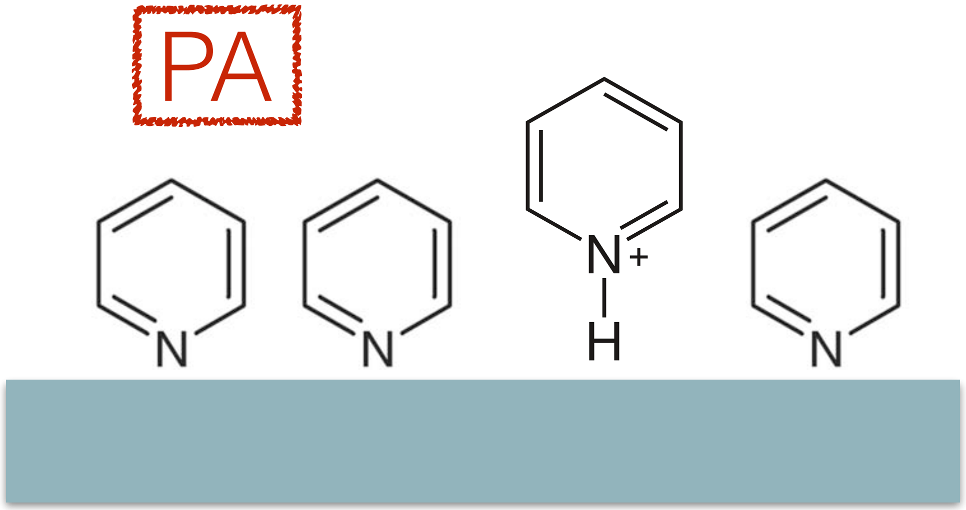
encapsulated polarising agent

particles covered with protecting groups



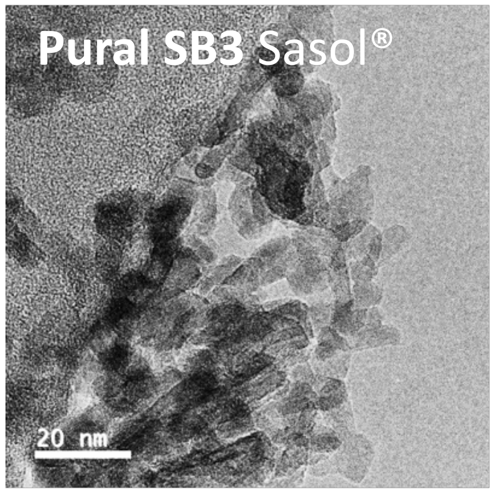
Dedicated formulation strategies for reactive surfaces

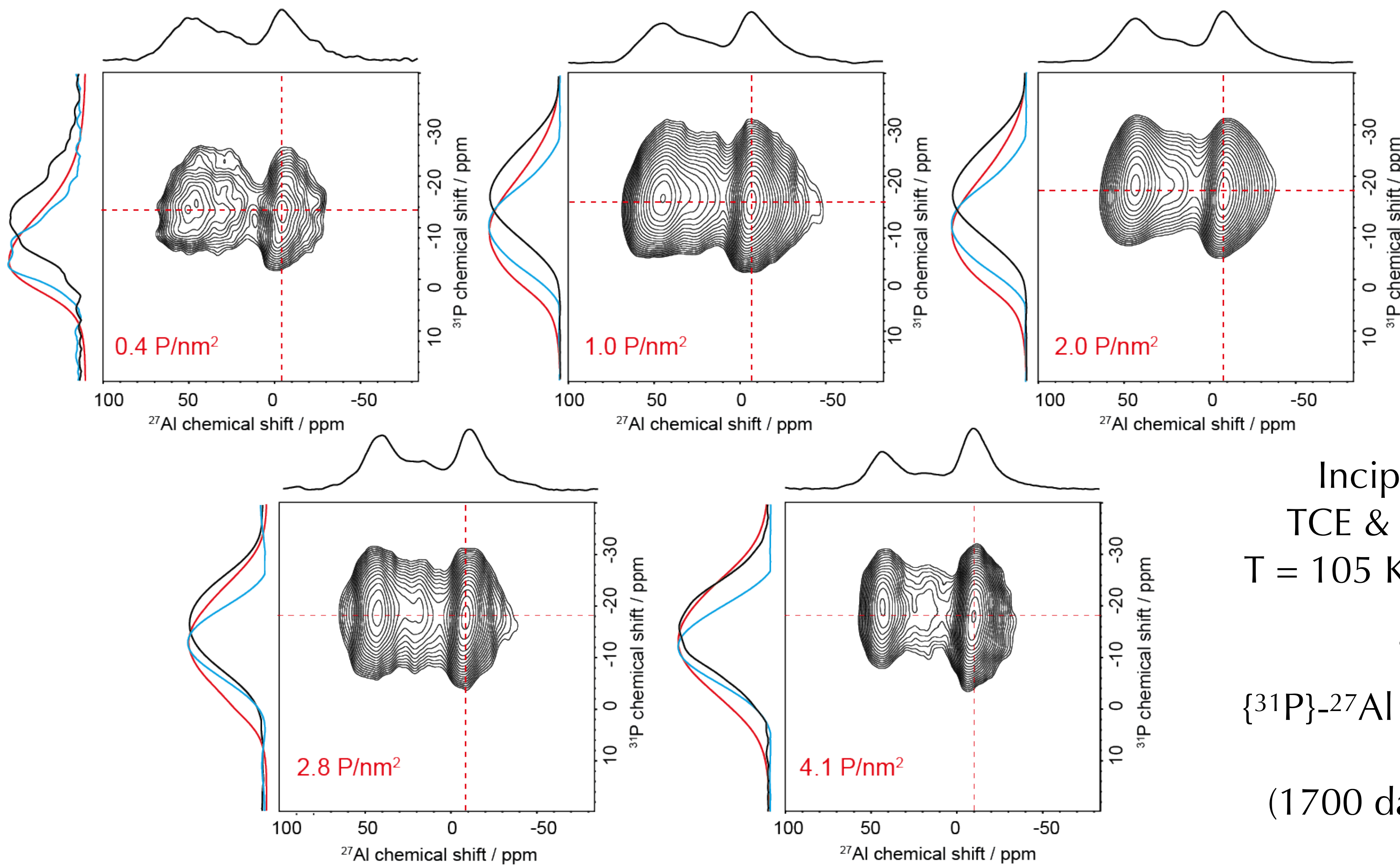




Liao, Copéret et al, *Chem. Sci.* **2017**, *8* (1), 416–422.
Yakimov, Copéret al, *Phys. Chem. Lett.* **2020**, 11 (9), 3401–3407.

Structural Characterization of Phosphate Species Adsorbed on γ-Alumina

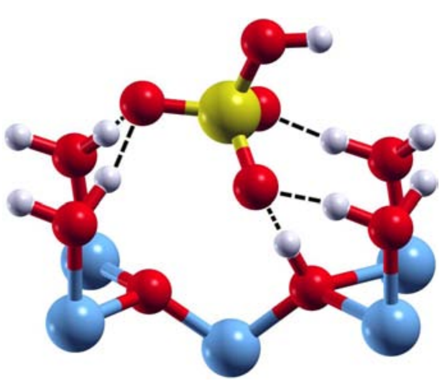


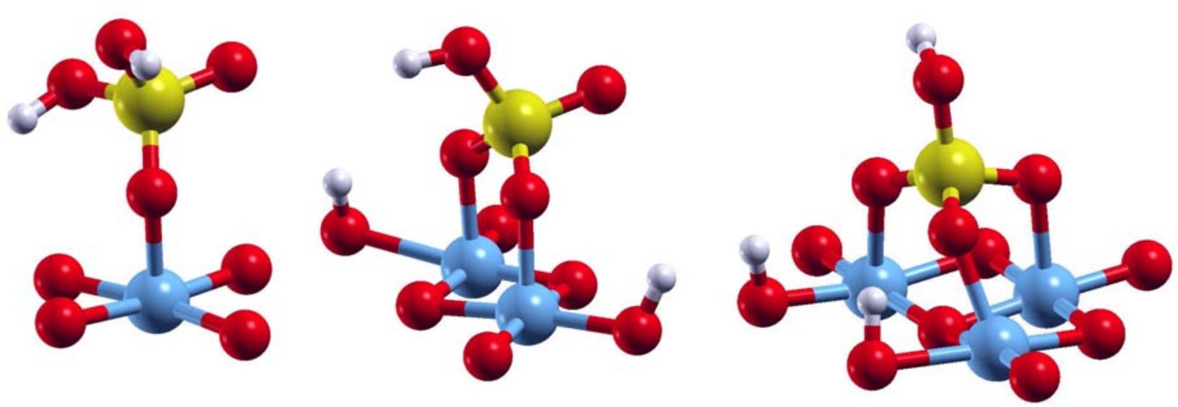


Incipient wetness with TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T

ε_H (solvent) ~ 100

{^{31}P}-^{27}Al D- and J-HMQC
4.5 hours
(1700 days without DNP)





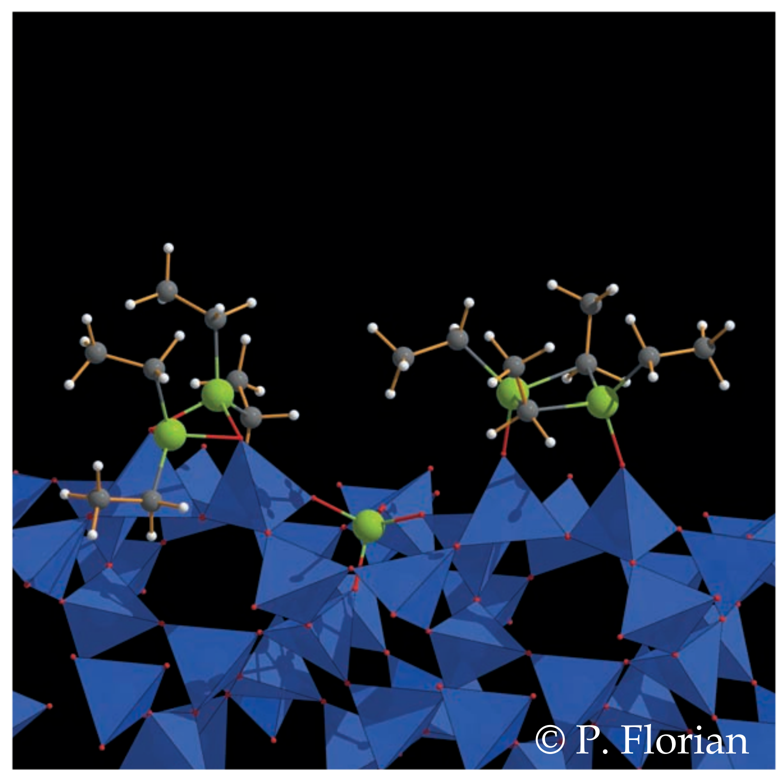
The presence of polyphosphates and of Al–O–P connectivities at the exposed facets of γAl_2O_3 is experimentally demonstrated.

Chaire ROAD4CAT

CARMEN
Caractérisation des matériaux pour les énergies nouvelles
Laboratoire Commun de Recherche

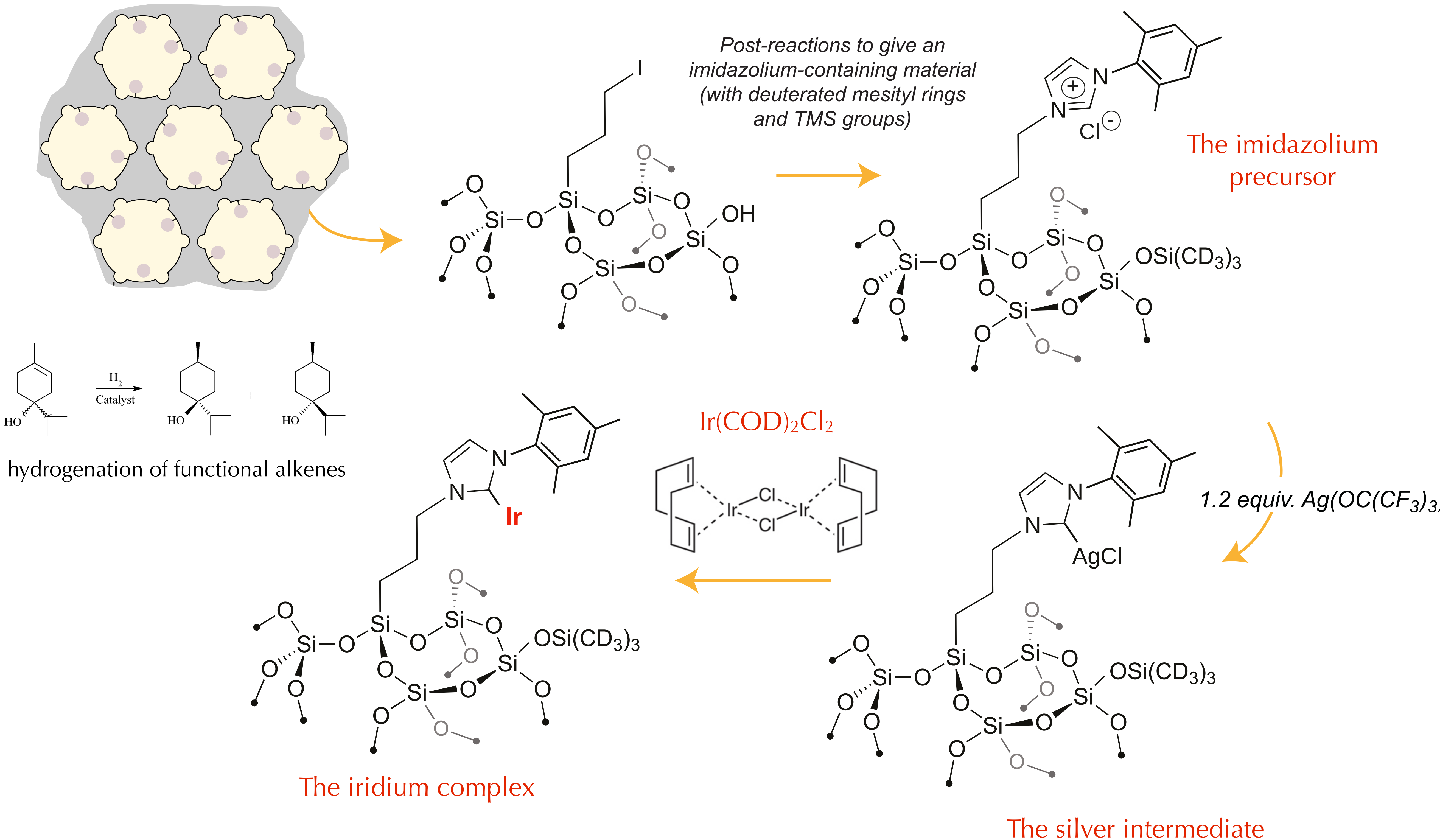
Huhn, A.; Wisser, D. […] Lesage, A.; Michel, C.; Raybaud, P. *ACS Catal.* **2021**, 11 (17), 11278–11292

DNP enhanced solid-state spectroscopy of supported molecular catalysts



DNP SENS of Supported Molecular Catalysts

N-Heterocyclic Carbene (NHC) materials of high catalytic performance



Romanenko, I. et al, Angew. Chem. Int. Ed. **2015**, 54 (44), 12937-12941.

Romanenko, I. et al, T, Chem. Eur. J. **2017**, 23 (64), 16171-16173.

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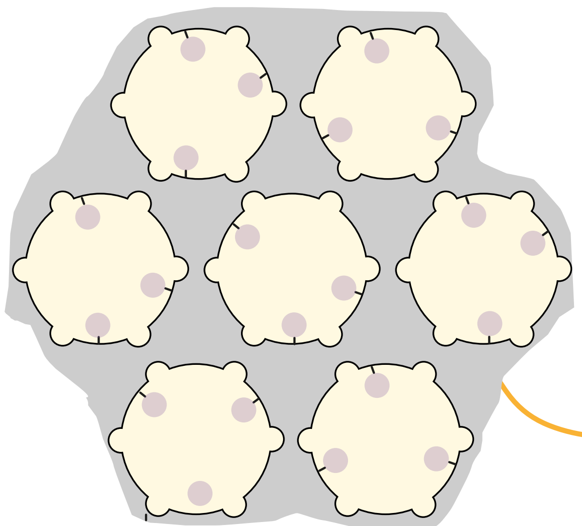
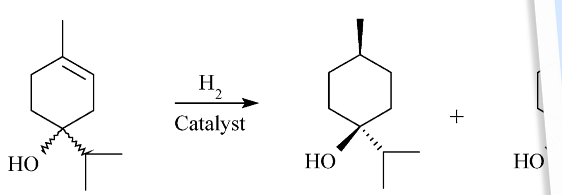
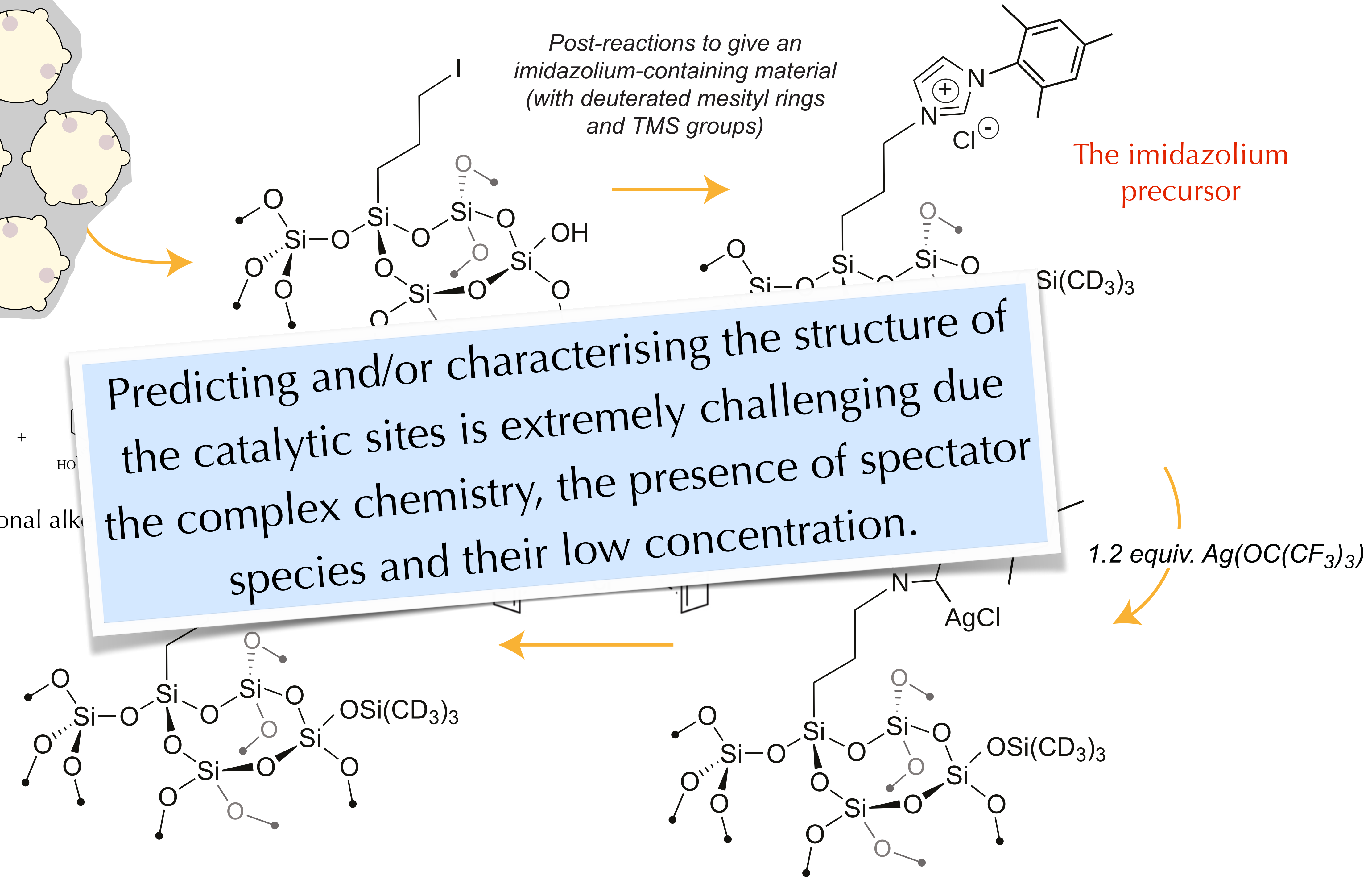




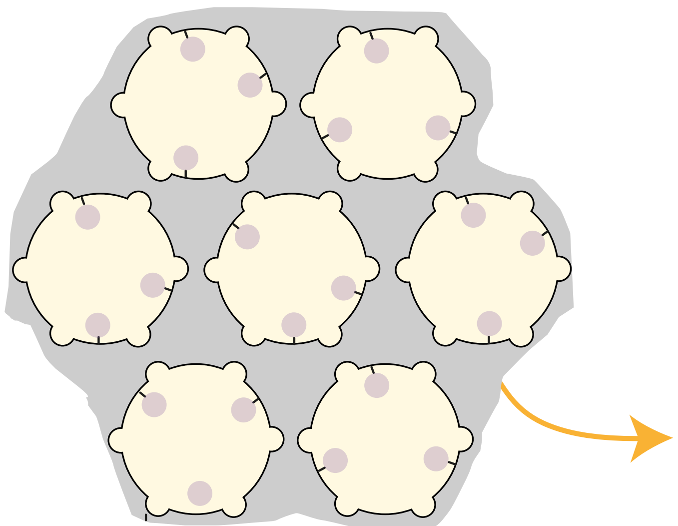
hydrogenation of functional alk



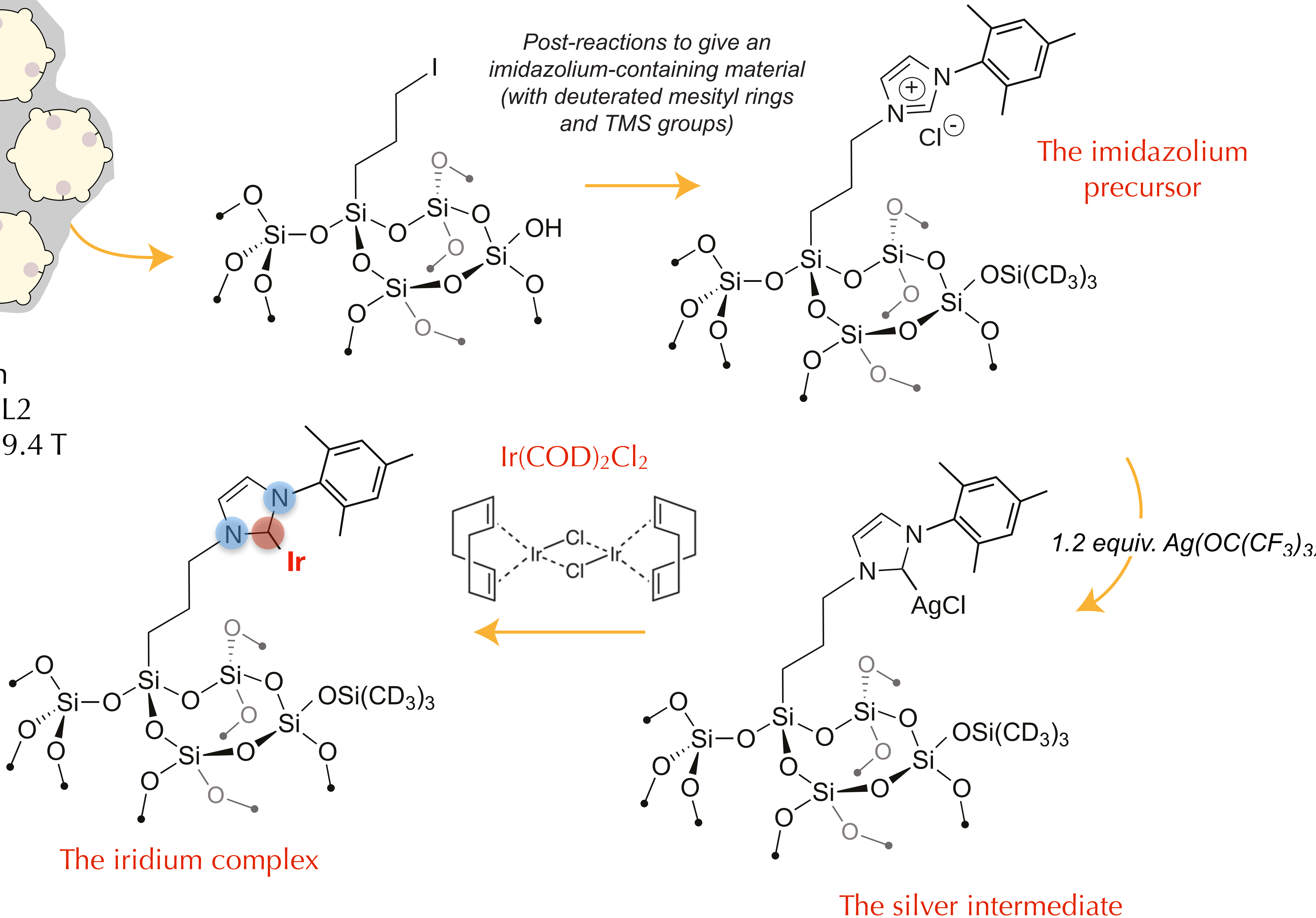
Predicting and/or characterising the structure of the catalytic sites is extremely challenging due the complex chemistry, the presence of spectator species and their low concentration.

DNP SENS of Supported Molecular Catalysts

N-Heterocyclic Carbene (NHC) materials of high catalytic performance



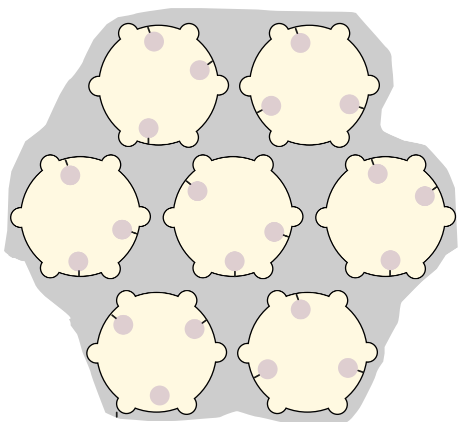
Incipient wetness with
TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T
ε_H (solvent) ~ 200



^{13}C labelling
^{15}N labelling

DNP SENS of Supported Molecular Catalysts

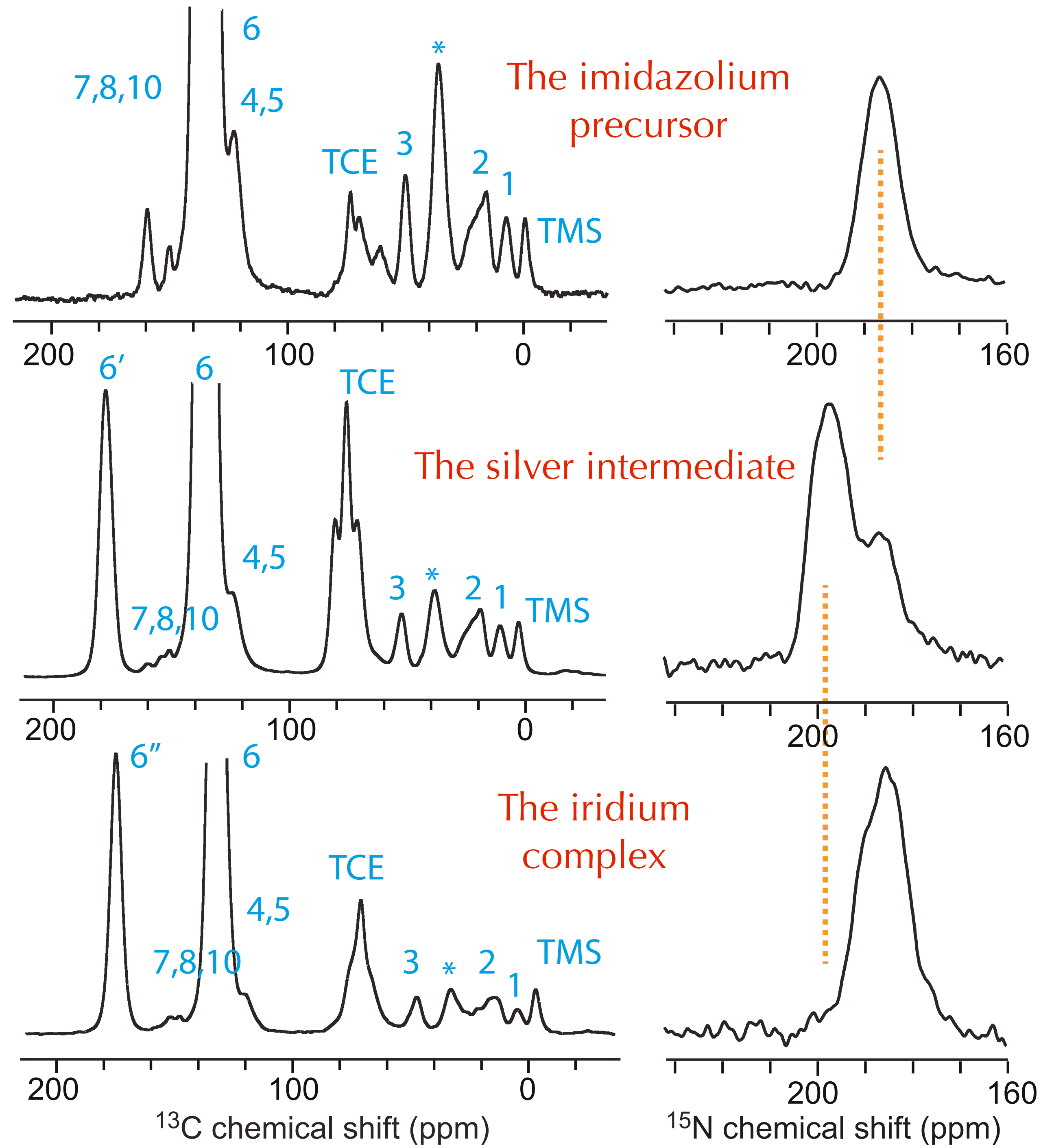
Expeditious acquisition of one- and two-dimensional spectra

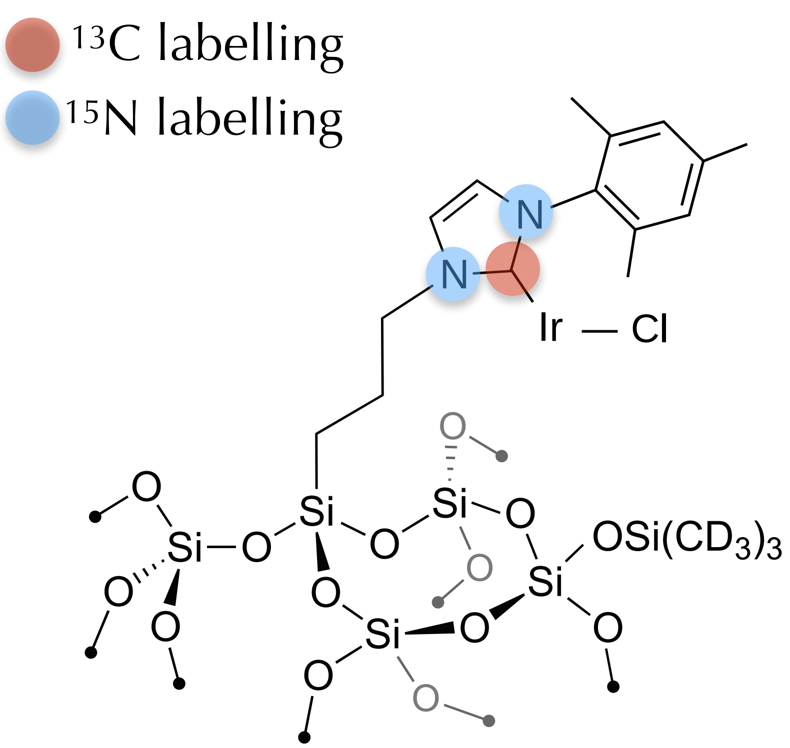


Incipient wetness with
TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T

ε_H (solvent) ~ 200

~ 2 min. for 1D spectrra
(~ hours without DNP)





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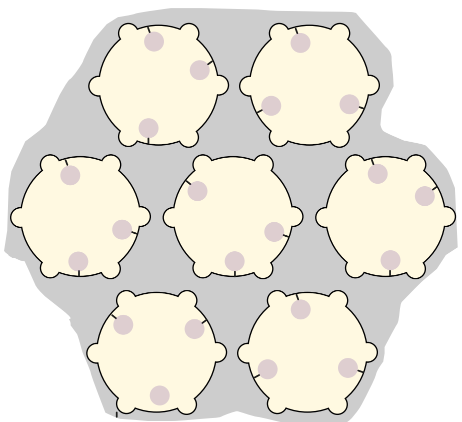
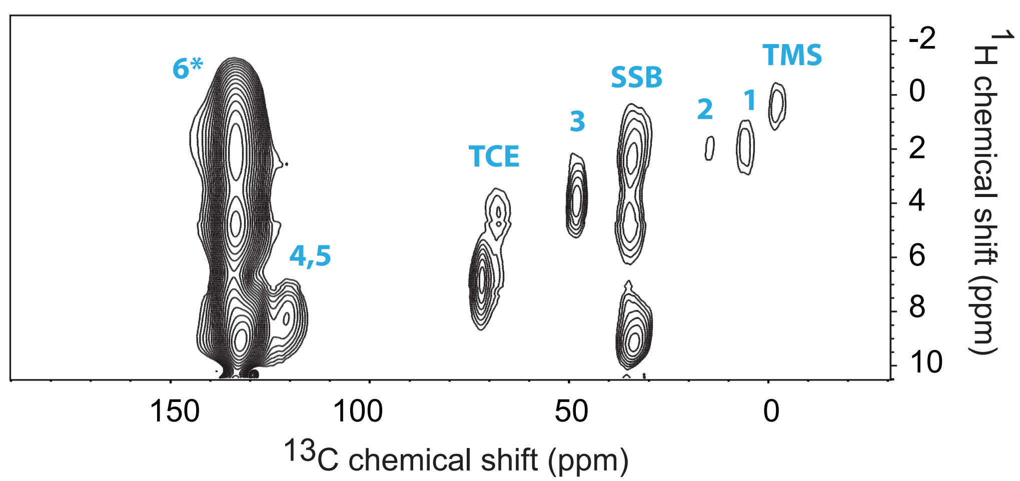


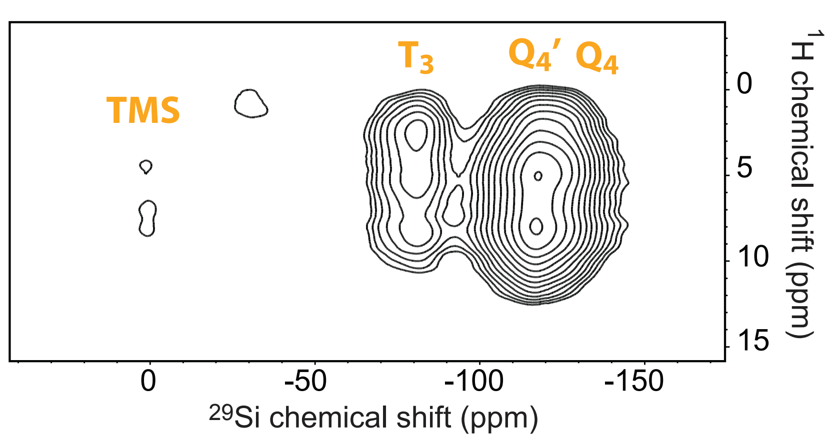
Incipient wetness with
TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T

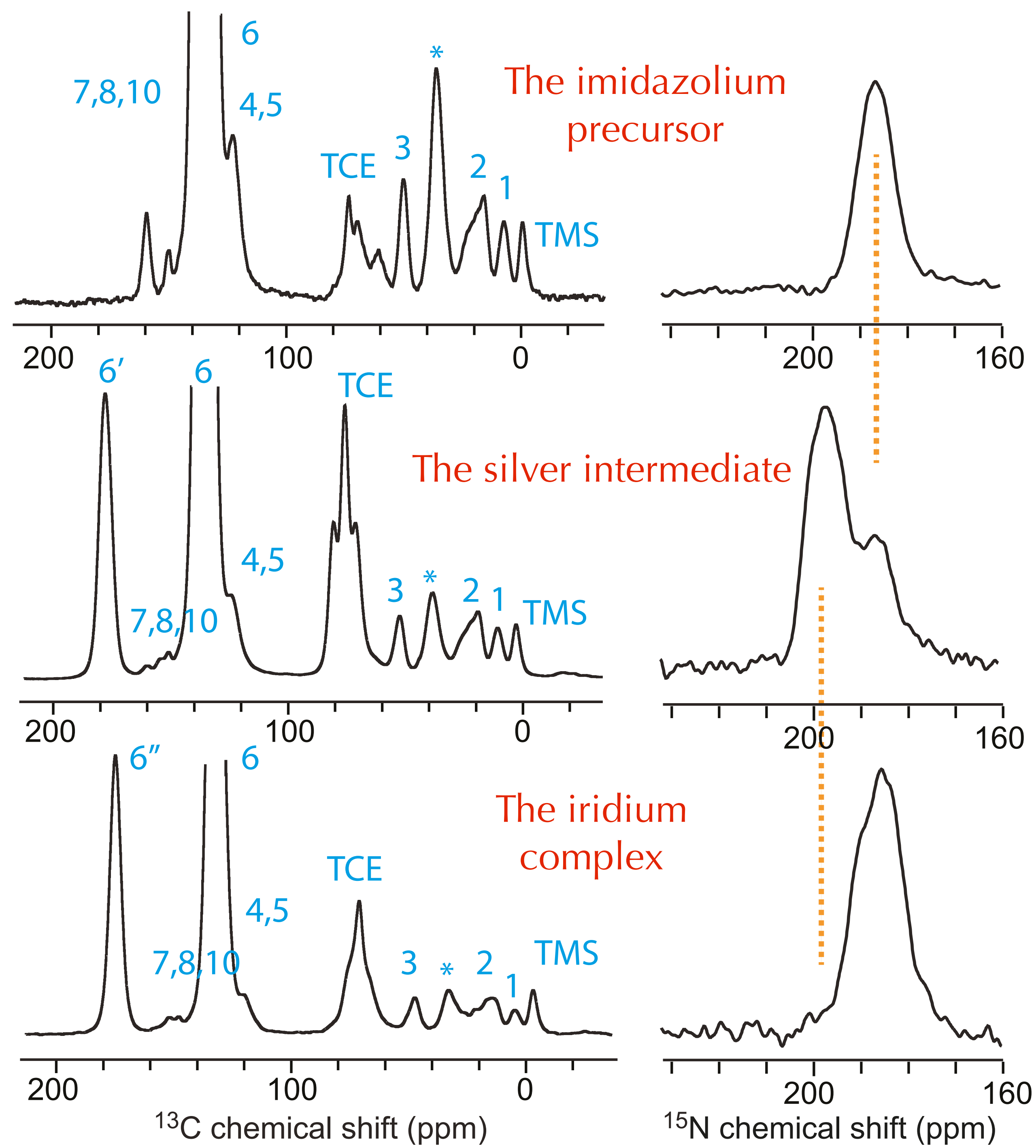
ε_H (solvent) ~ 200

~ 2 min. for 1D spectrra
(~ hours without DNP)

~ 2 hours for a 2D spectrum
(~ 1 month without DNP)

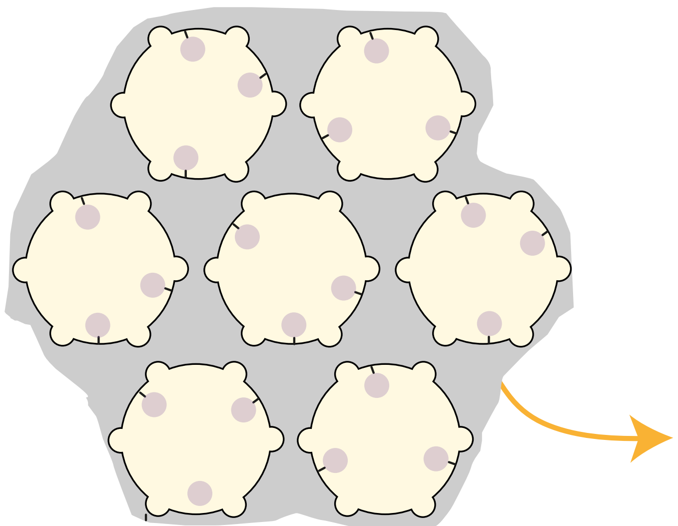


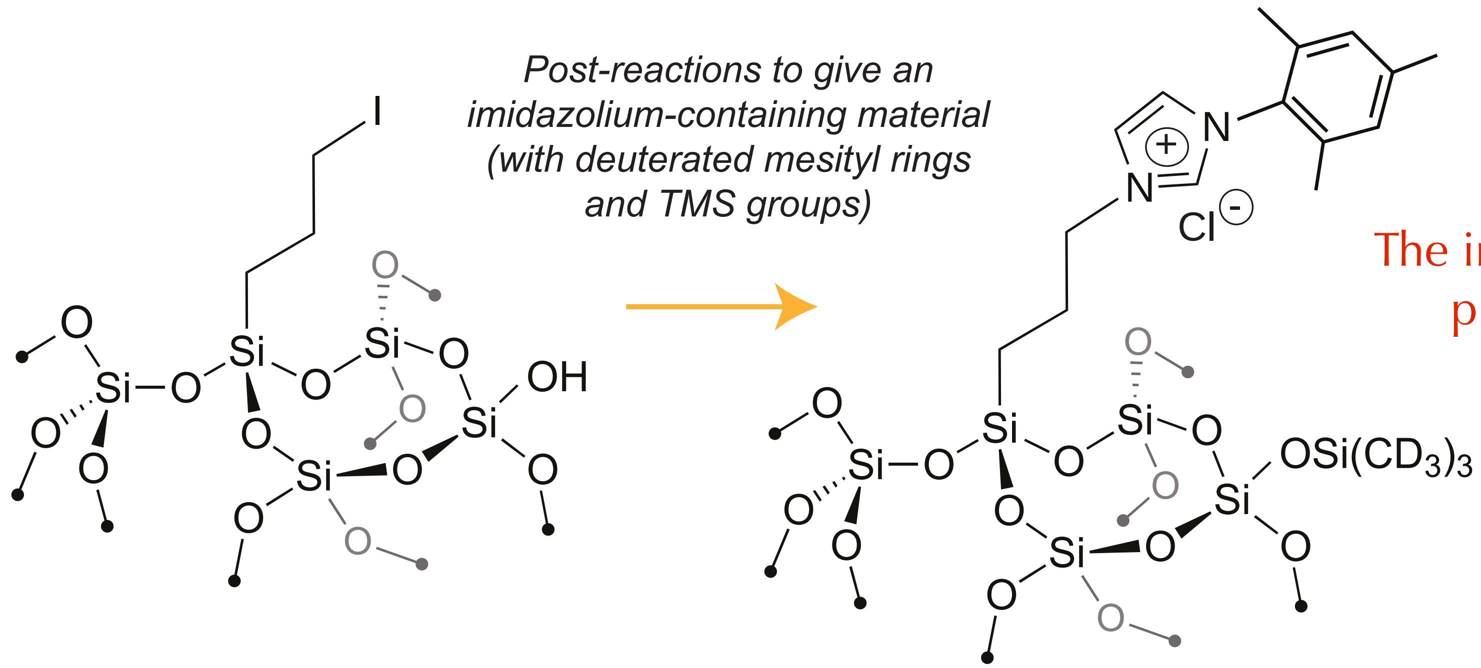




DNP SENS of Supported Molecular Catalysts

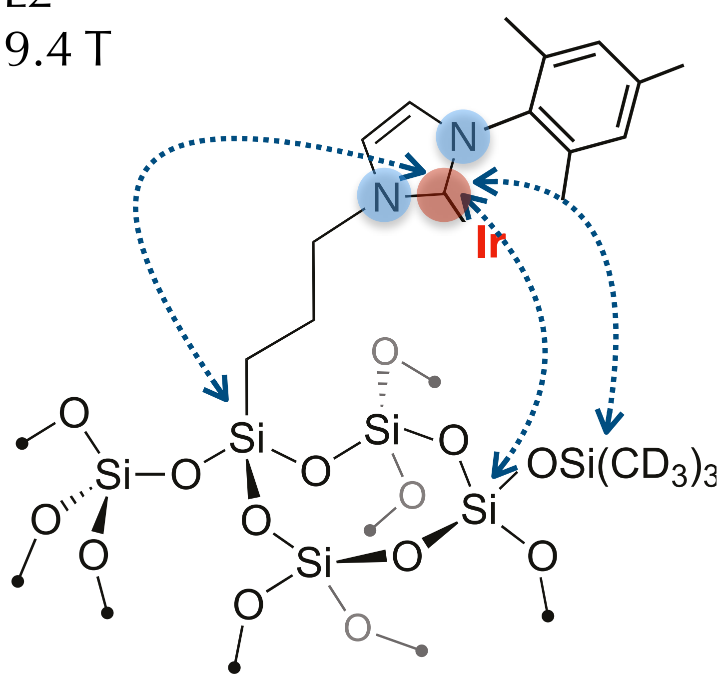
Site-selective measurements of distances





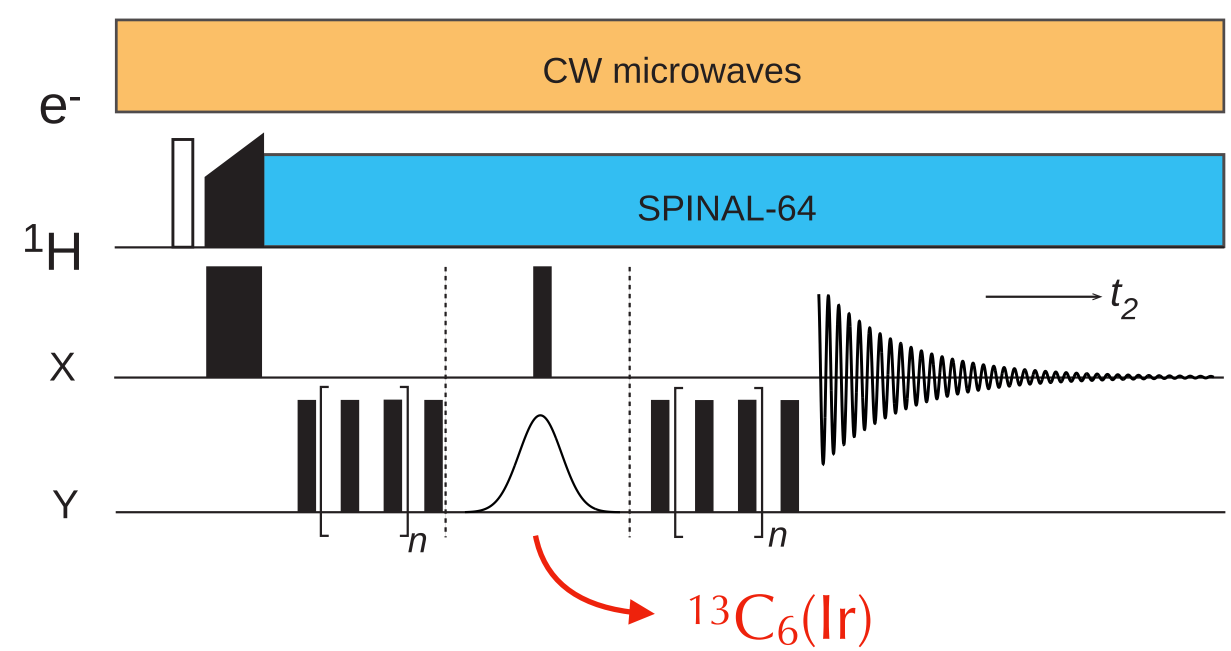
The imidazolium precursor

Incipient wetness with
TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T
ε_H (solvent) ~ 200



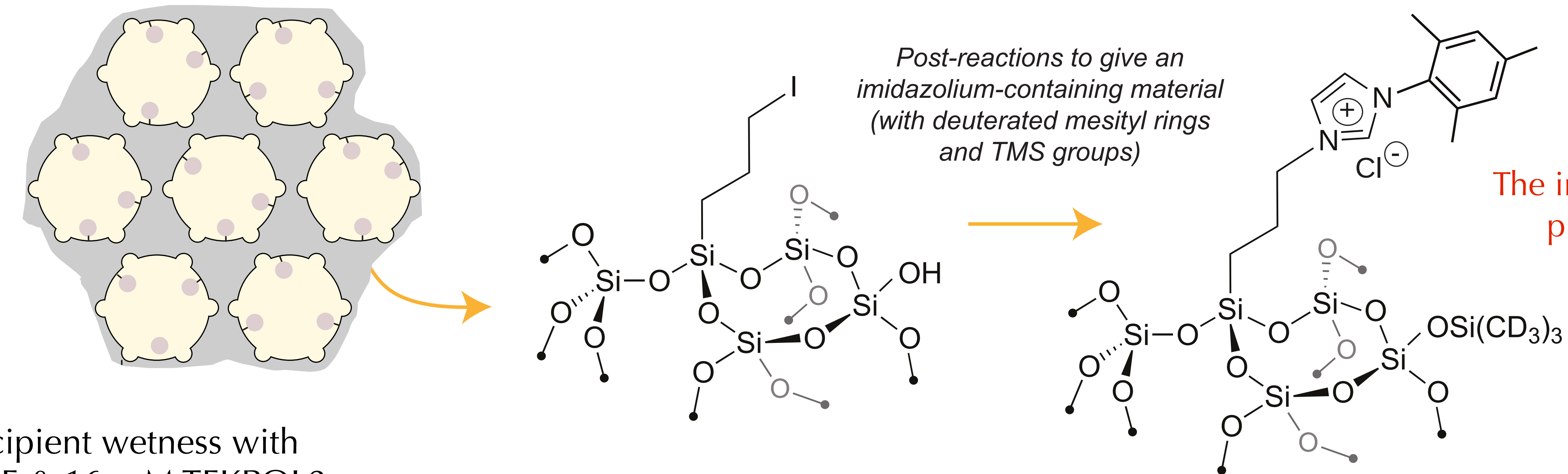
The iridium complex

^{13}C labelling
^{15}N labelling



DNP SENS of Supported Molecular Catalysts

Site-selective measurements of distances



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Incipient wetness with
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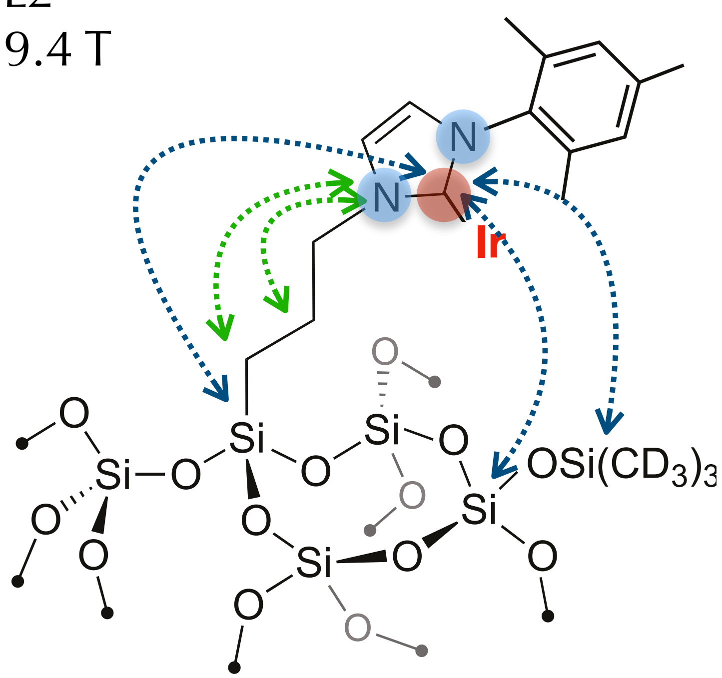

The iridium complex

^{13}C labelling
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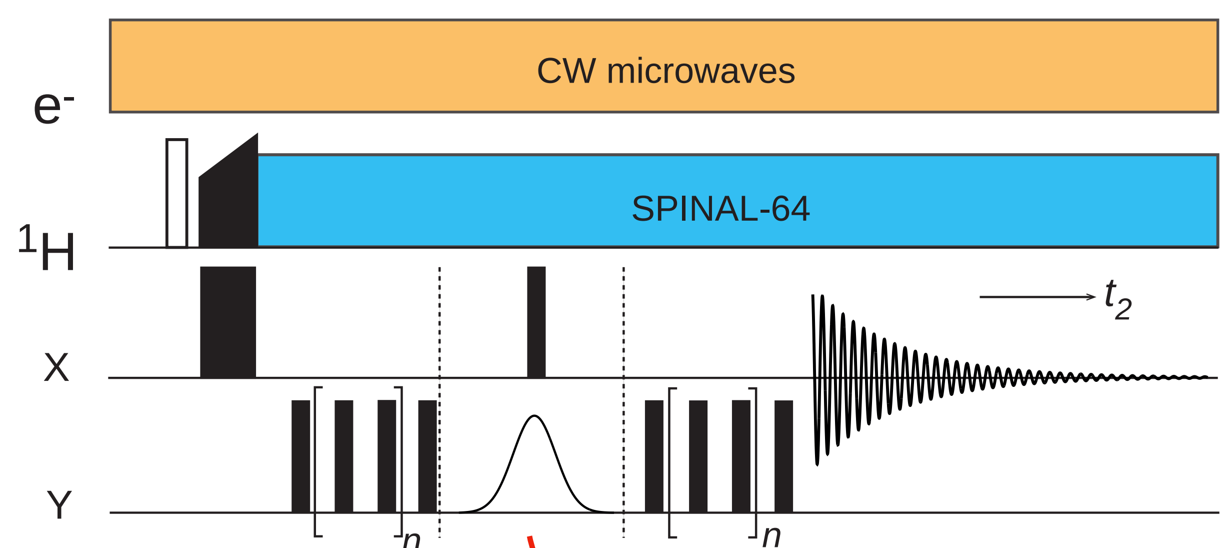
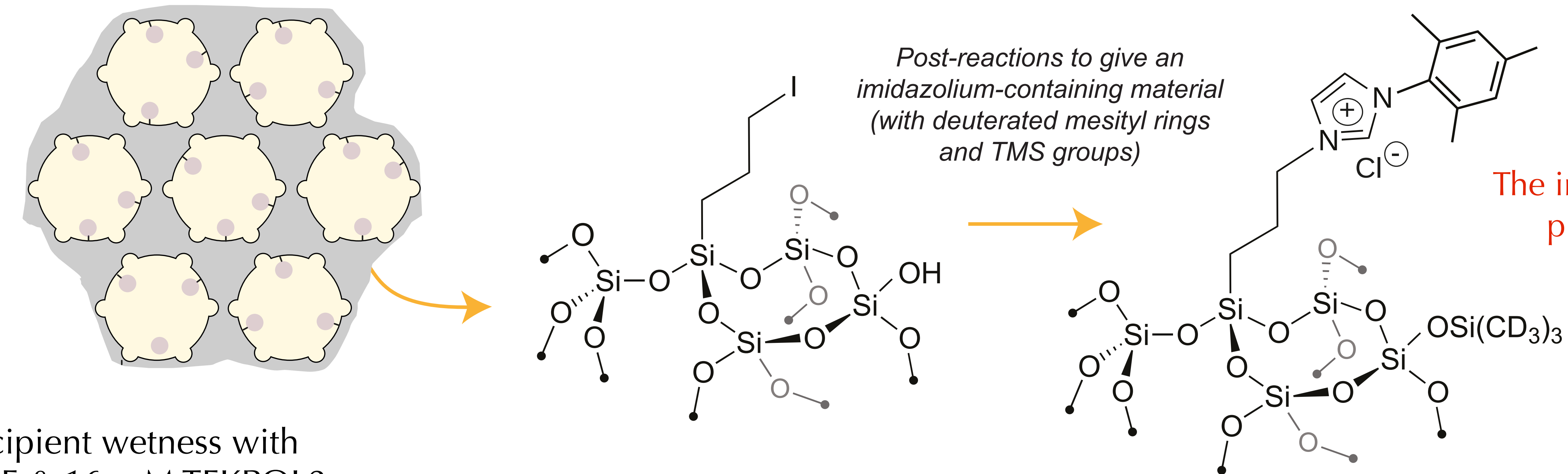


$^{13}C_6$(Ir)

DNP SENS of Supported Molecular Catalysts

Site-selective measurements of distances



The imidazolium precursor

Incipient wetness with
TCE & 16 mM TEKPOL2
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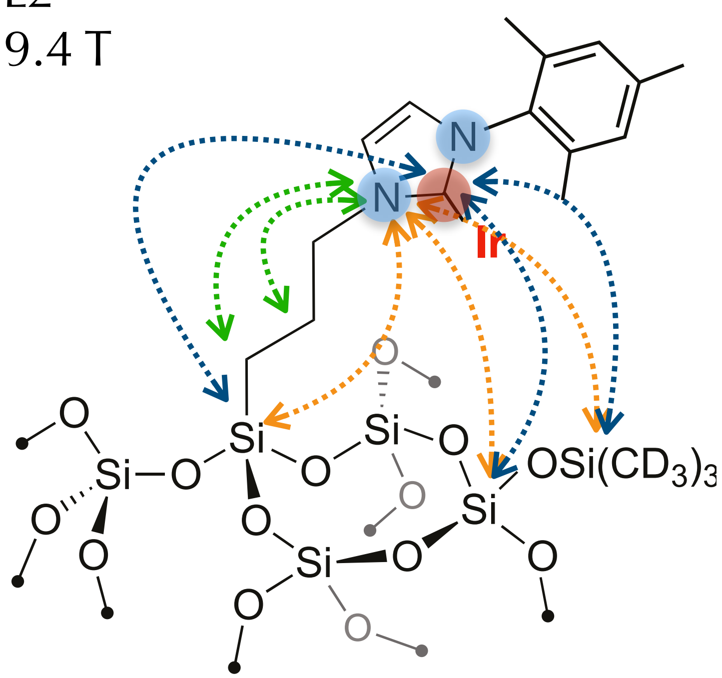
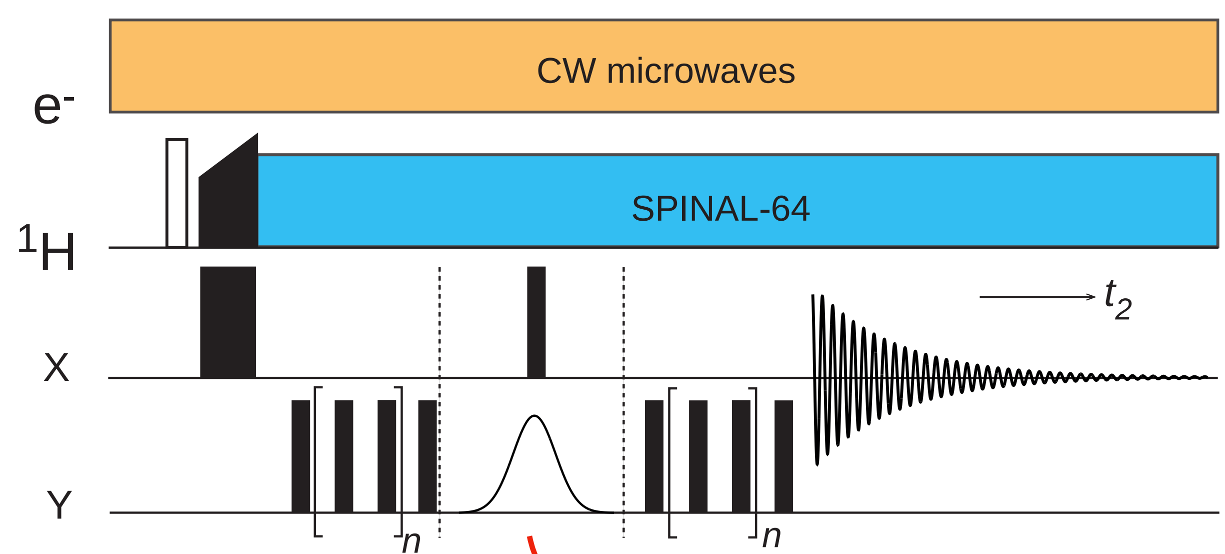
ε_H (solvent) ~ 200



The iridium complex

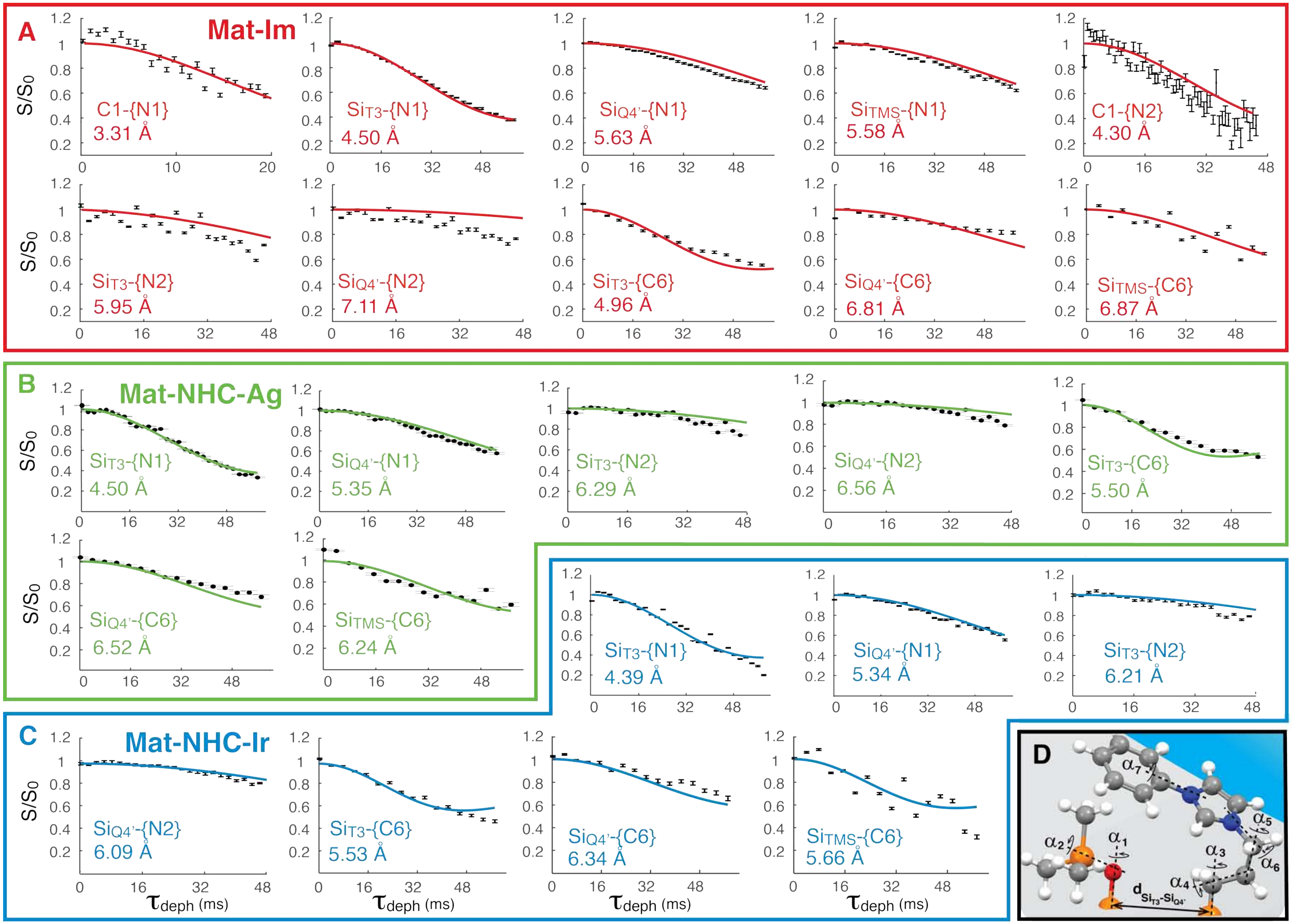
^{13}C labelling
^{15}N labelling



$^{13}C_6$(Ir)

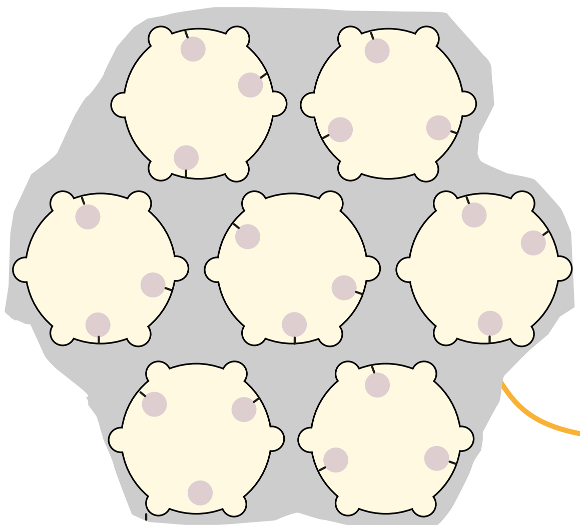
DNP SENS of Single-Site Heterogeneous Catalysts

A set of structural constraints at all stages of the synthetis

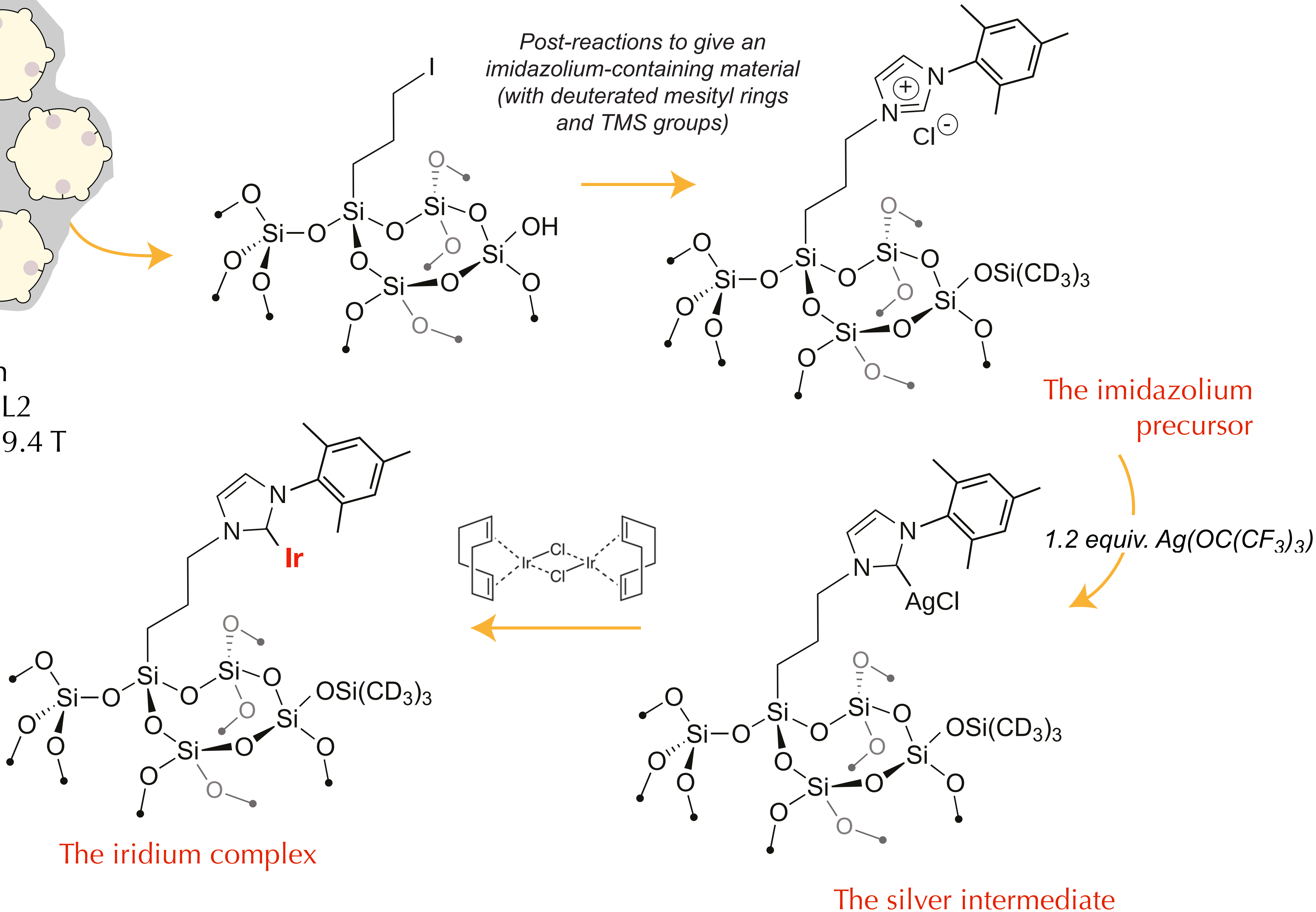


DNP SENS of Supported Molecular Catalysts

Ir-NHC hybrid materials of high catalytic hydrogenation performance

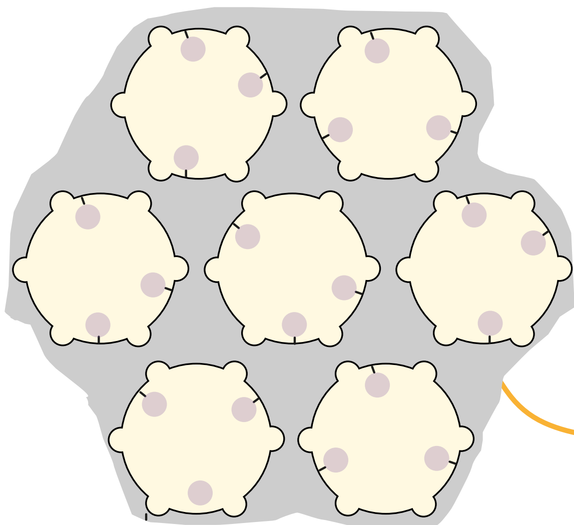


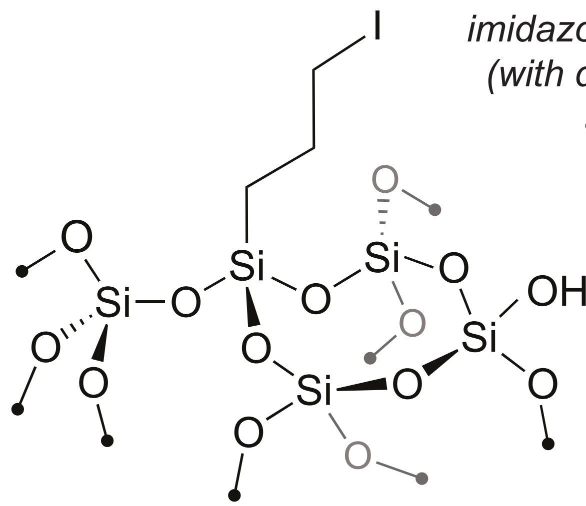
Incipient wetness with
TCE & 16 mM TEKPOL2
T = 105 K, 263 GHz, 9.4 T



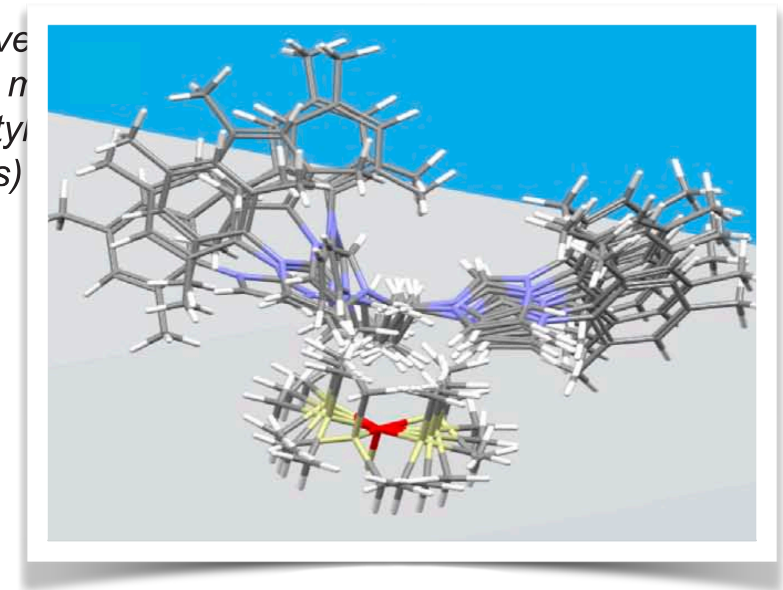
DNP SENS of Supported Molecular Catalysts

A complete atomic-scale structural description of all surface sites



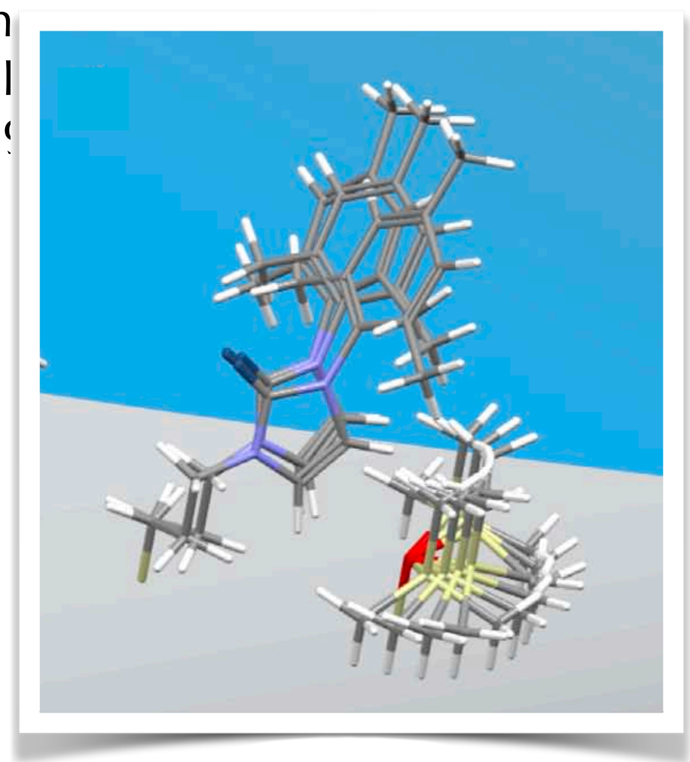


Post-reactions to give imidazolium-containing m (with deuterated mesityl and TMS groups)

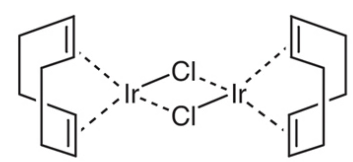


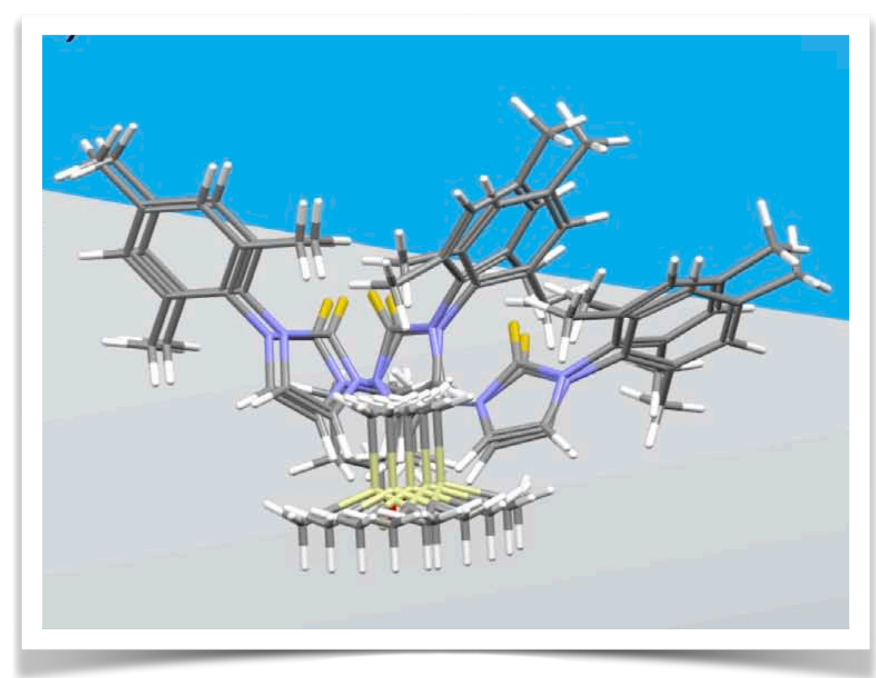
The imidazolium precursor

Incipient wetness with TCE & 16 mM TEKPOl
T = 105 K, 263 GHz, 9



The iridium complex

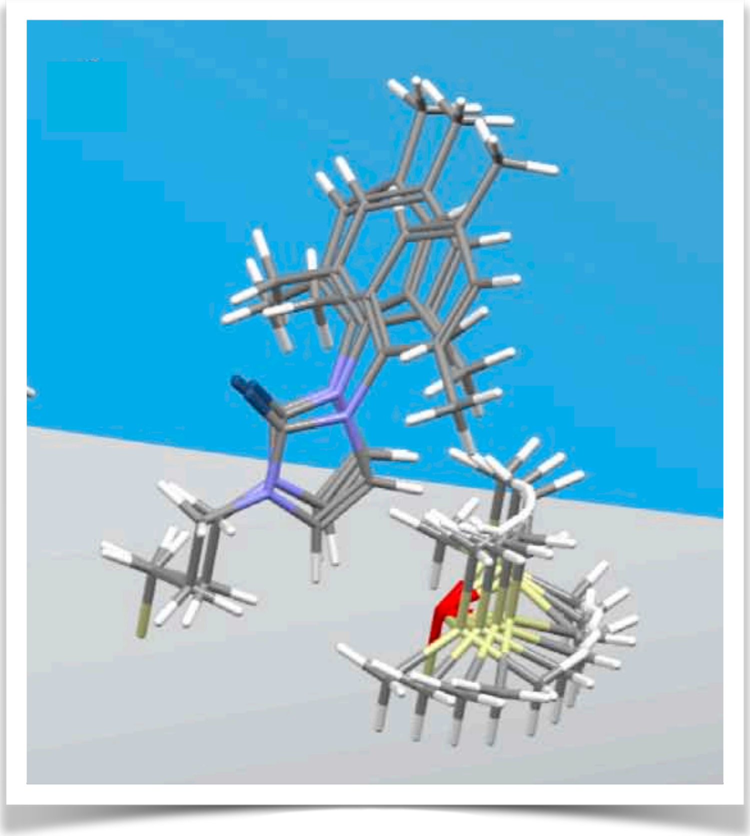




The silver intermediate

DNP SENS of Supported Molecular Catalysts

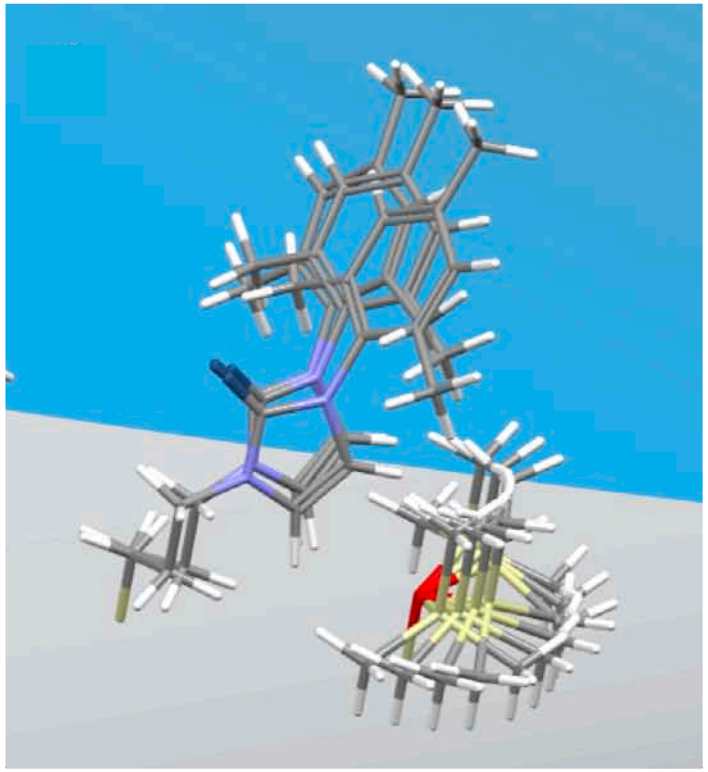
Ir-NHC hybrid materials of high catalytic hydrogenation performance



- ☐ completely disordered structures?
- ☐ distributions rather flat on the surface?
- ☐ distributions pointing into solution?
- ☑ a well-defined structure pointing into solution?

DNP SENS of Supported Molecular Catalysts

Ir-NHC hybrid materials of high catalytic hydrogenation performance



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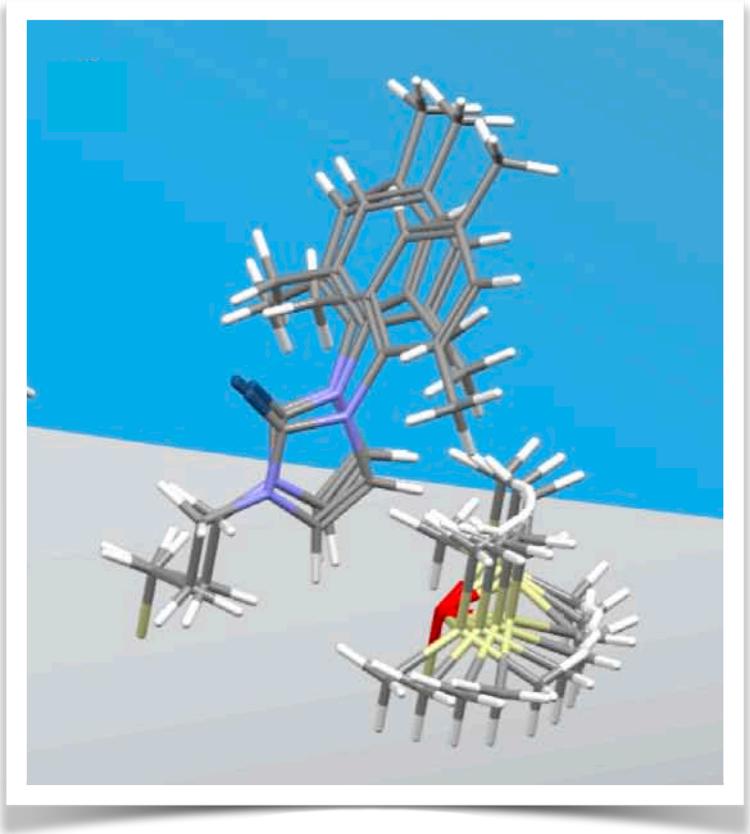
This can't be the final structure!

EXAFS data point towards the presence of carbon and chlorine atoms around the Ir center (and not of oxygens).

DNP SENS of Supported Molecular Catalysts

Ir-NHC hybrid materials of high catalytic hydrogenation performance



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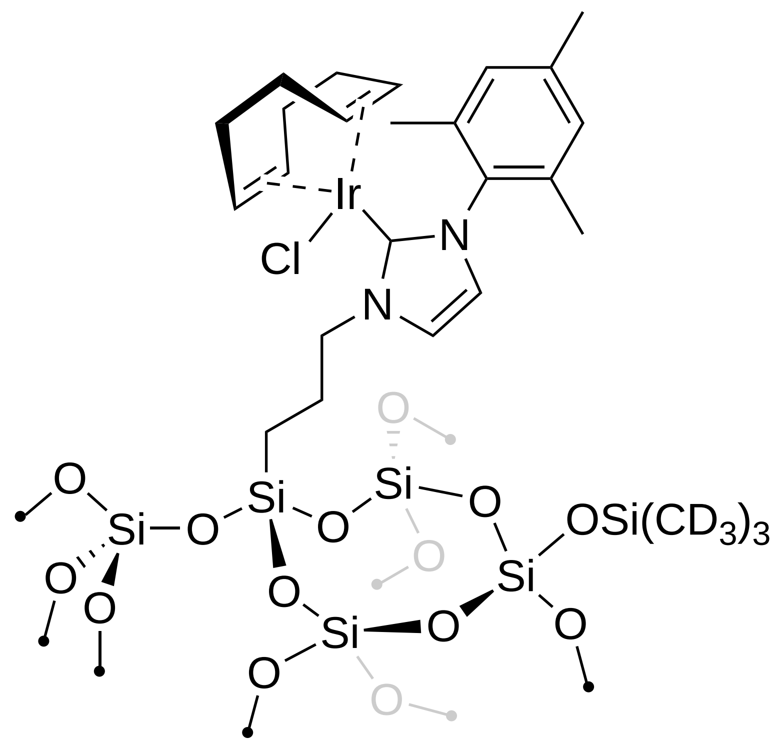

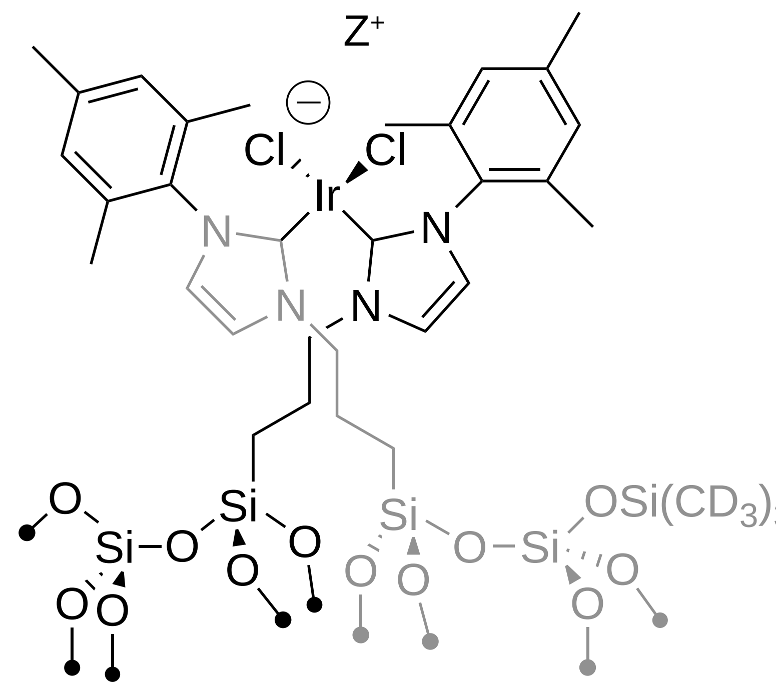

DNP SENS reveals a well-defined structure with two different (unexpected) coordination environments.

Jabbour, R.; Renom-Carrasco, M.; Chan, K. W.; Völker, L.; Berruyer, P.; Wang, Z.; Widdifield, C. M.; Lelli, M.; Gajan, D.; Copéret, C.; Thieuleux, C.; Lesage, A., *J. Am. Chem. Soc.* **2022,** *144* (23), 10270-10281.

DNP SENS of Supported Molecular Catalysts

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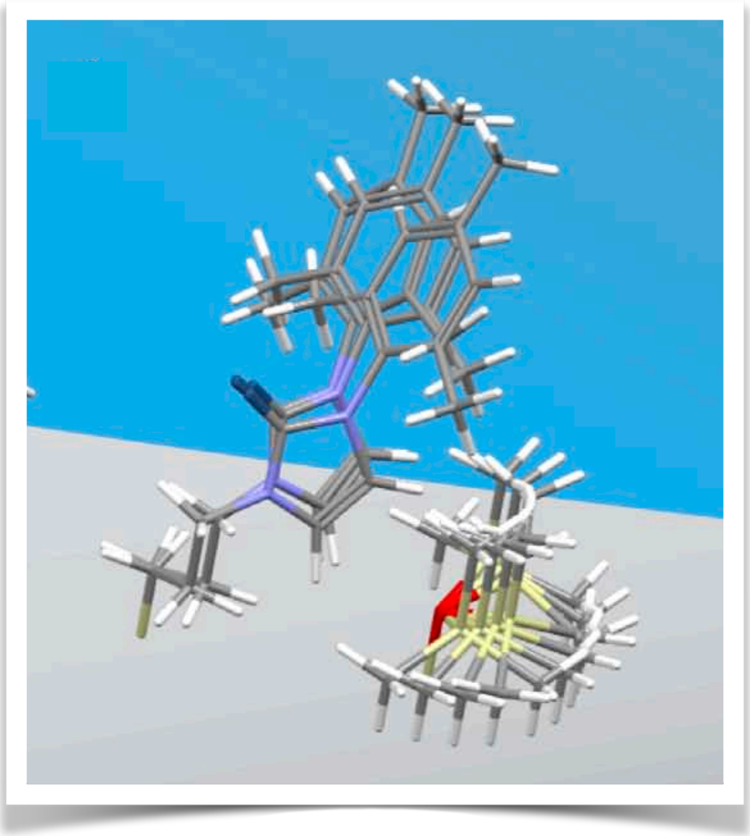

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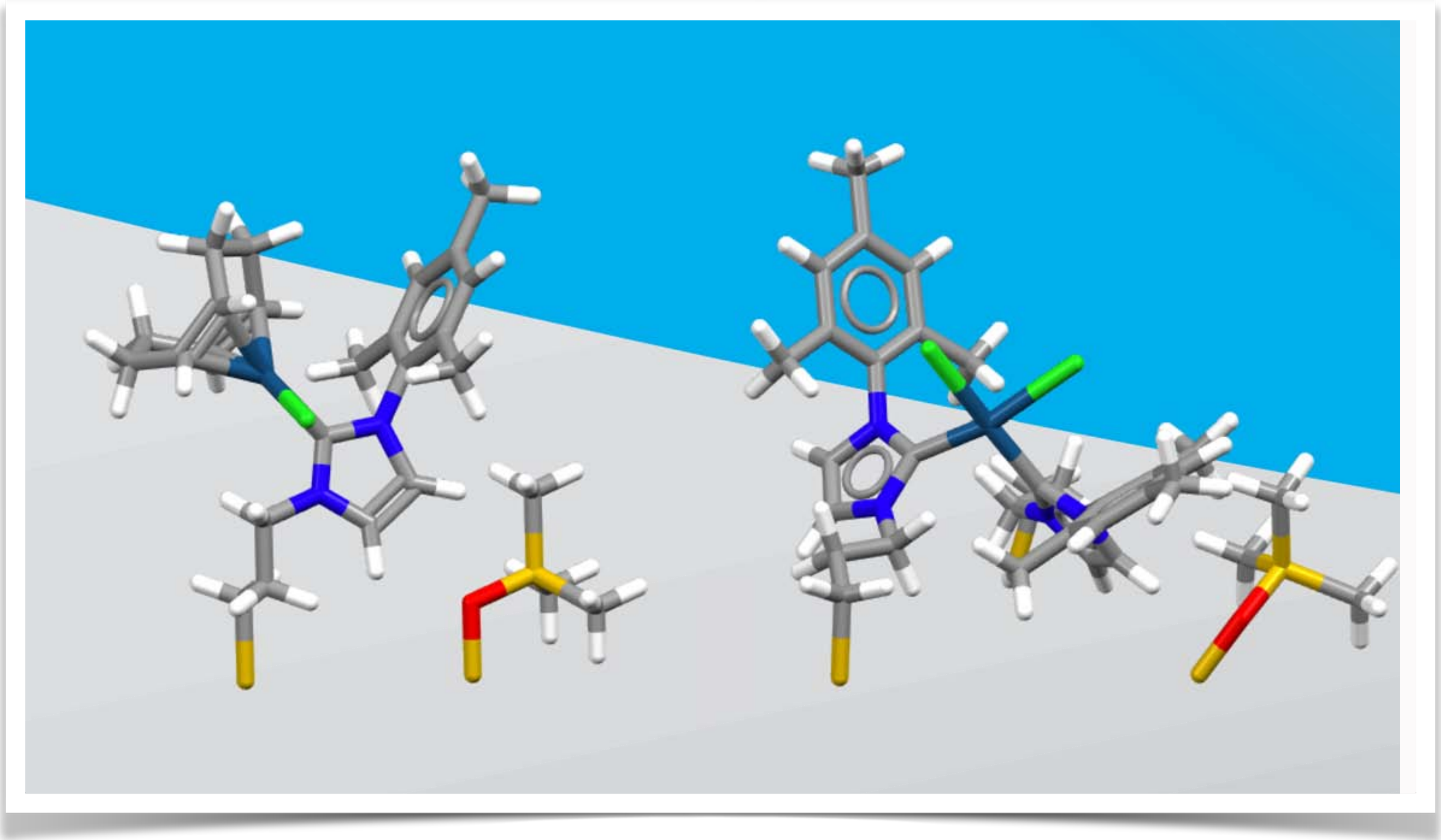

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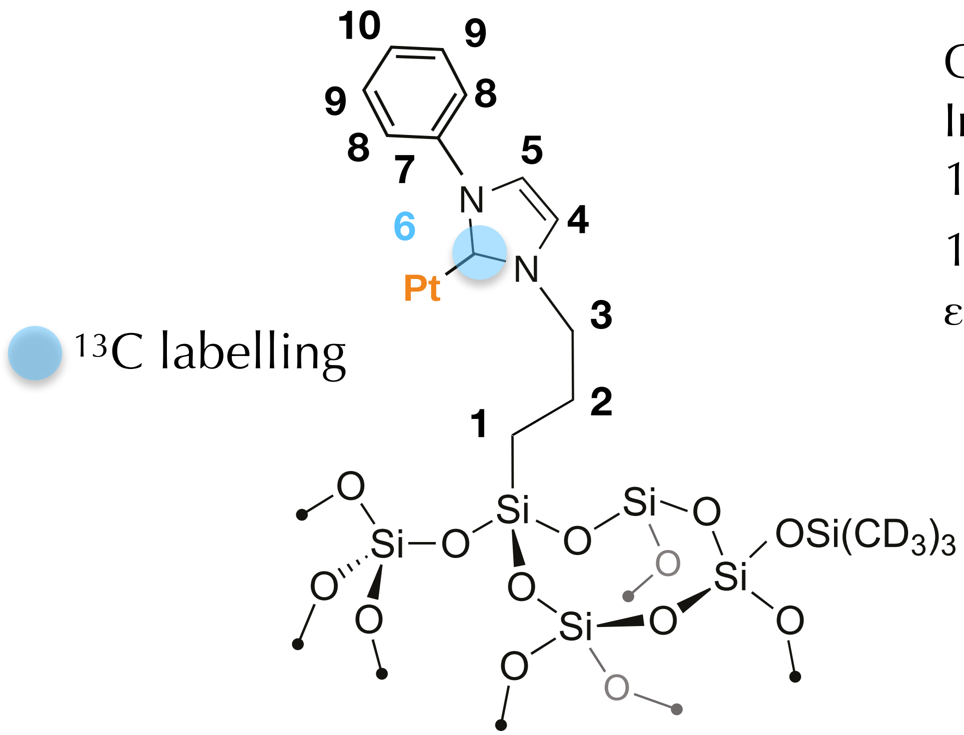
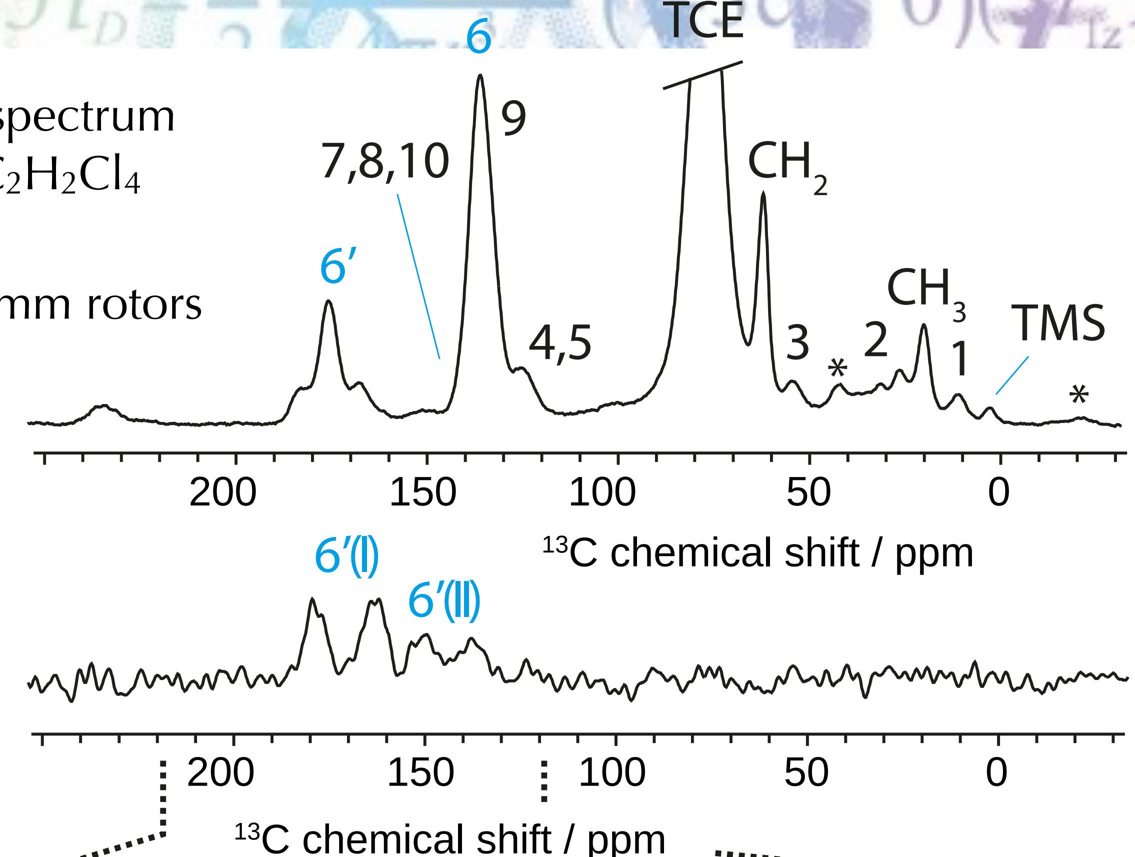
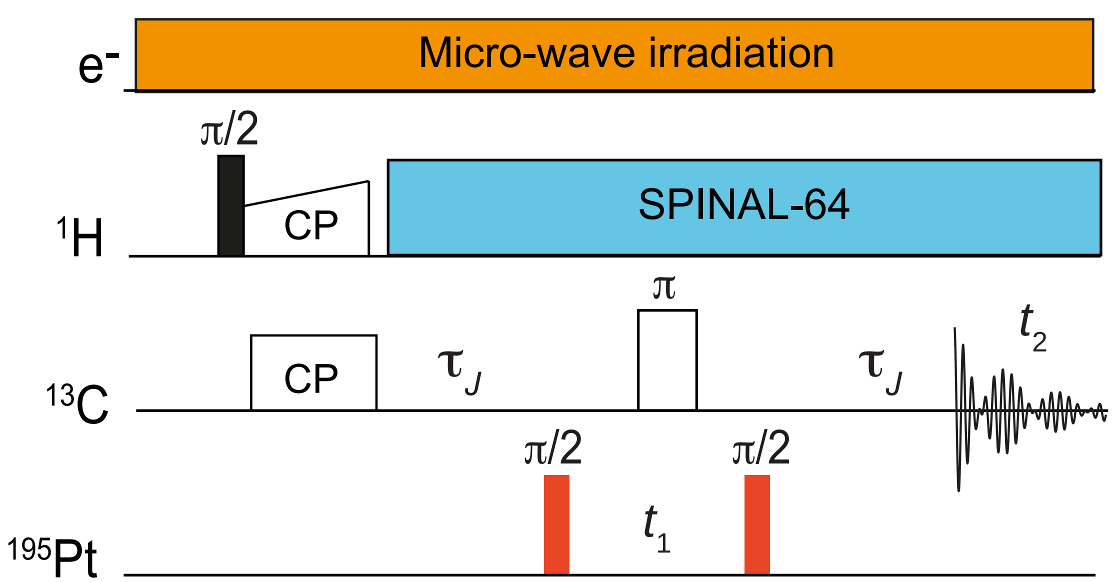
Indirectly-Detected ^{195}Pt Wideline NMR under Fast MAS Frequencies and DNP

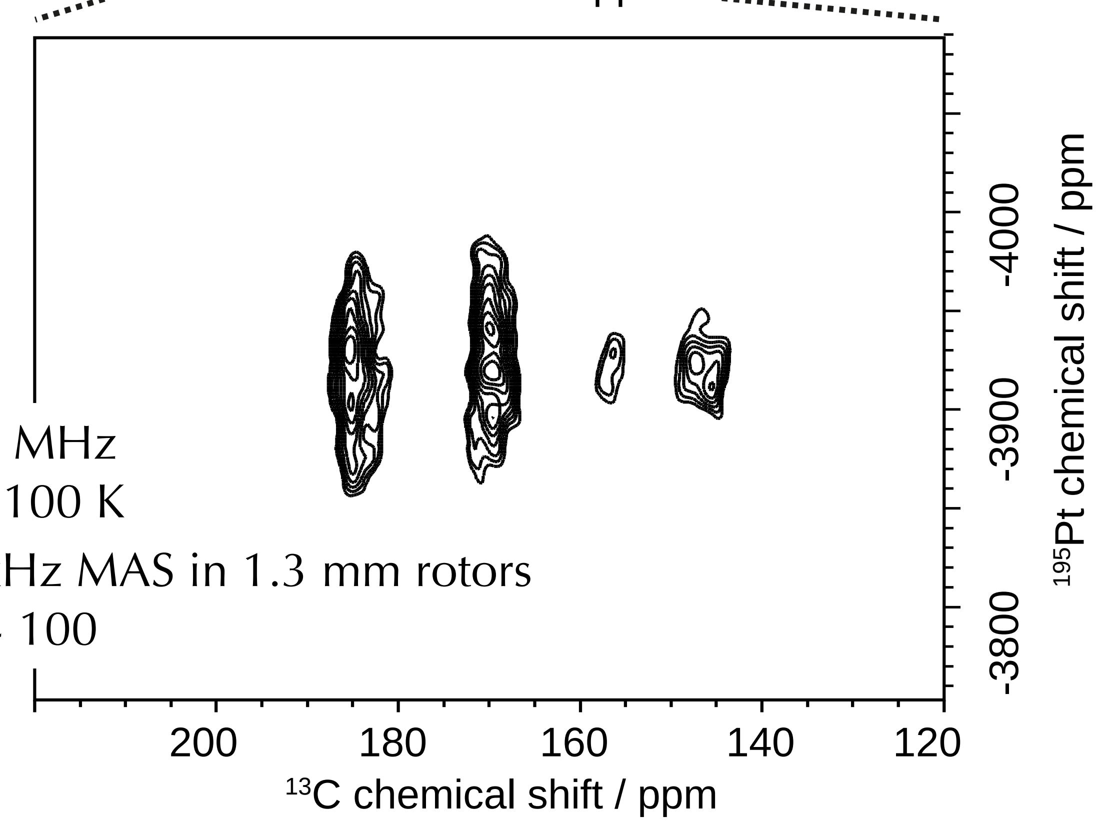


Carbon-13 CPMAS spectrum
Impregnation with $C_2H_2Cl_4$
10 mM TEKPOL
10 kHz MAS in 3.2 mm rotors
$\varepsilon_H \sim 64$



J-HMQC ^{13}C-^{195}Pt experiment

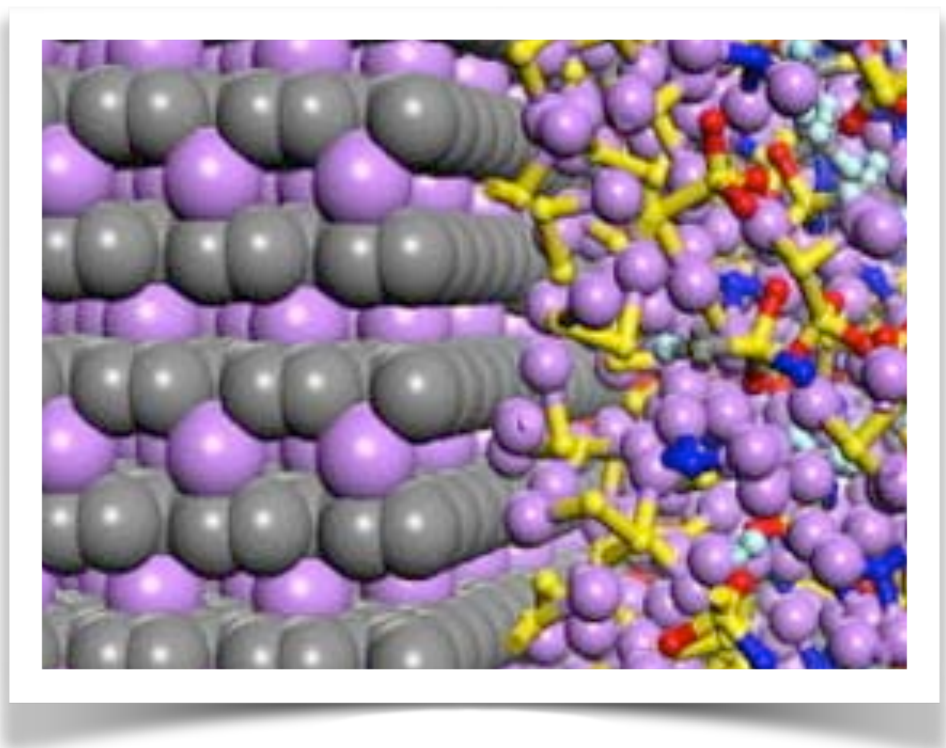




400 MHz
T = 100 K
36 kHz MAS in 1.3 mm rotors
$\varepsilon_H \sim 100$

Venkatesh, A., Lund, A., […] Copéret, C., Lesage, A. and Rossini A. *J. Am. Chem. Soc.* **2020**, 142, 18936–18945.
Venkatesh, A.,Gioffre, D., […] Lesage, A., Copéret, C., and Rossini A. *J. Am. Chem. Soc.* accepted.

DNP enhanced solid-state spectroscopy of bulk functional materials



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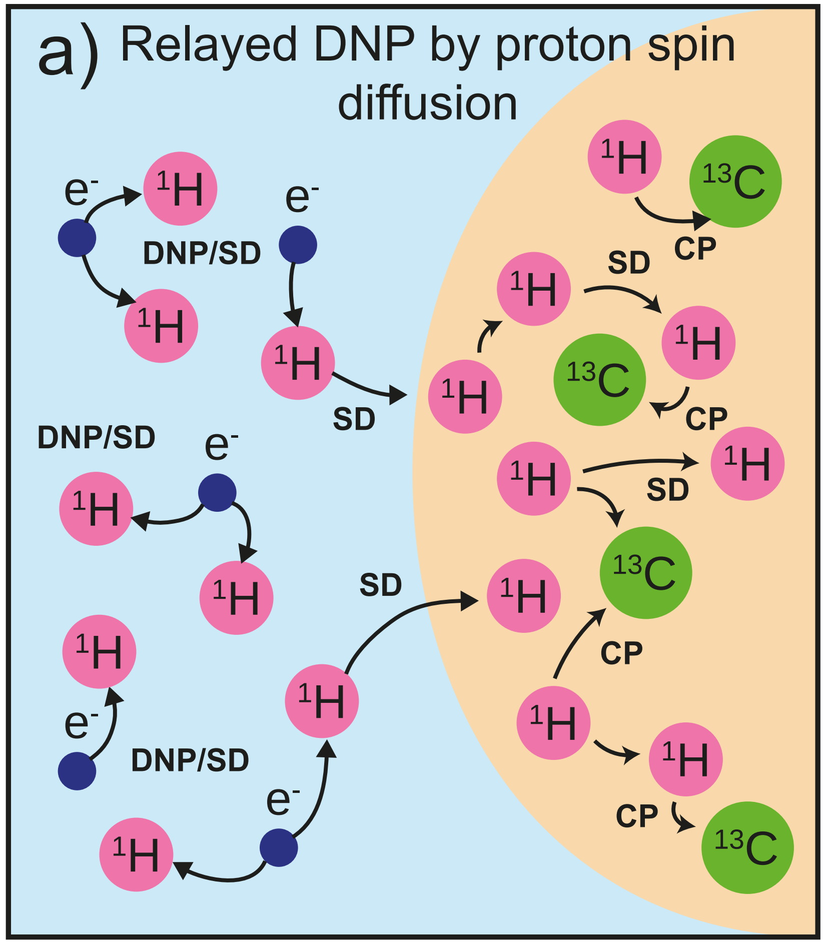

(a) Rossini, A. J.; Zagdoun, A.; […] Gajan, D.; Copéret, C.; Lesage, A.; Emsley, L.. *J. Am. Chem. Soc.* **2012**, *134* (40), 16899–16908.
(b) Björgvinsdóttir, S.; Walder, B. J.; Pinon, A. C.; Emsley, L. *J. Am. Chem. Soc.* **2018**, *140*, 7946–7951.
(c) Wolf, T.; Kumar, S.; Singh, H.; Chakrabarty, T.; Aussenac, F.; Frenkel, A. I.; Major, D. T.; Leskes, M. *J. Am. Chem. Soc.* **2019**, *141*, 451–462.

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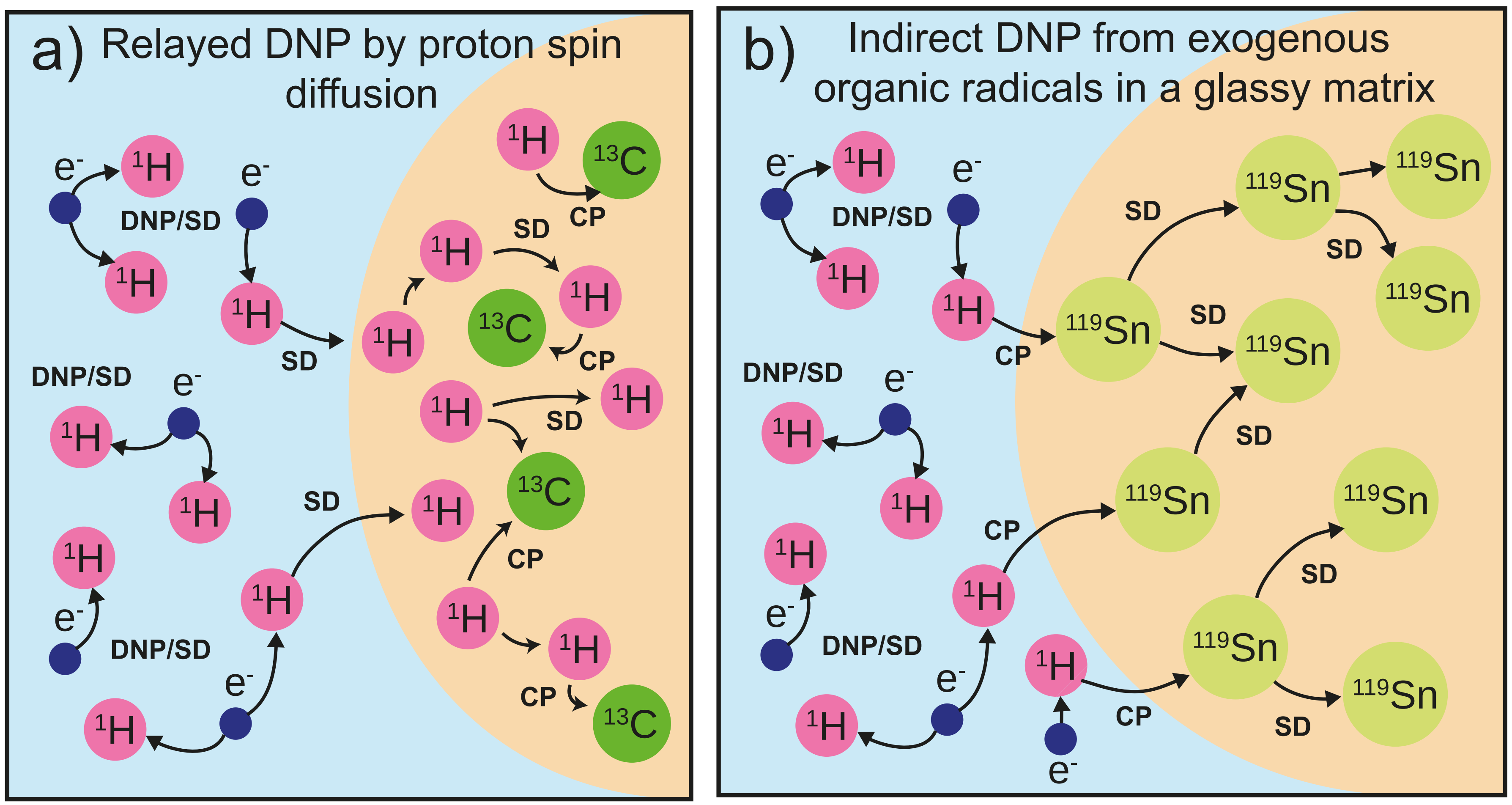

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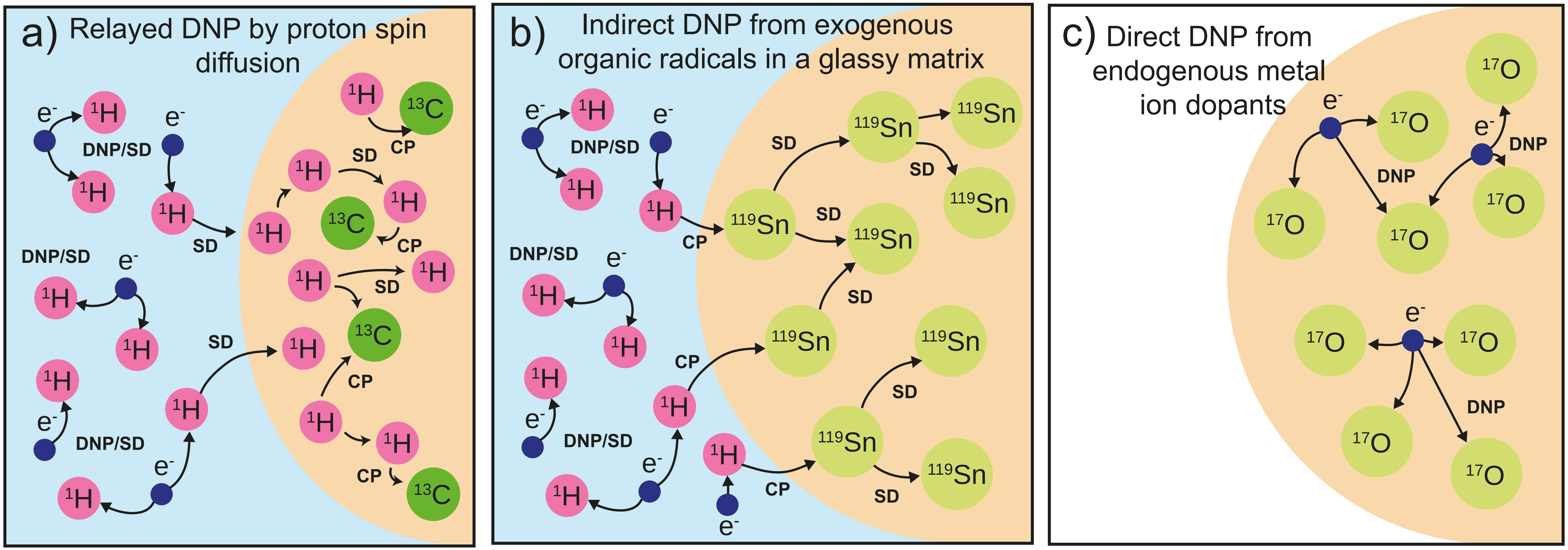

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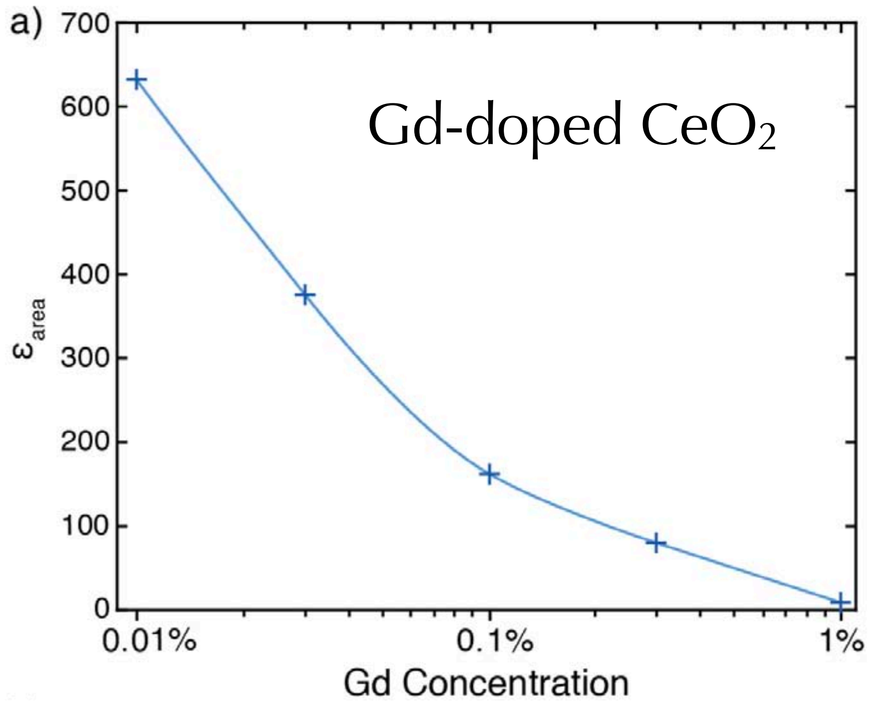
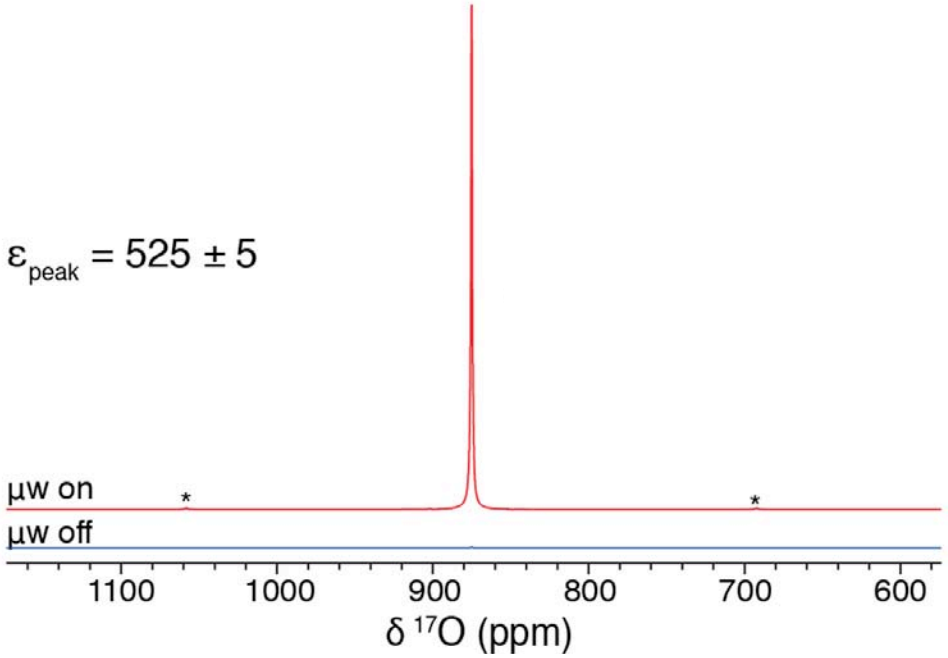
Endogeneous DNP NMR of Inorganic Materials





Hope, M. A.; Bjorgvinsdottir, S.; Halat, D. M.; Menzildjian, G.; Wang, Z.; […] ; Lesage, A.; Lelli, M.; Emsley, L.; Grey, C. P. *J. Phys. Chem. C* **2021**, *125* (34), 18799–18809.

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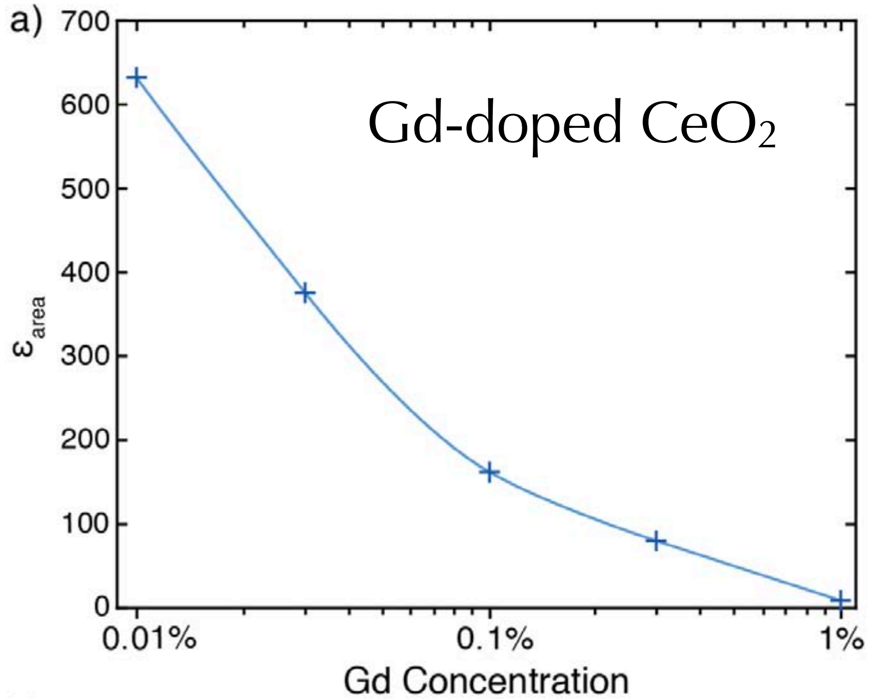
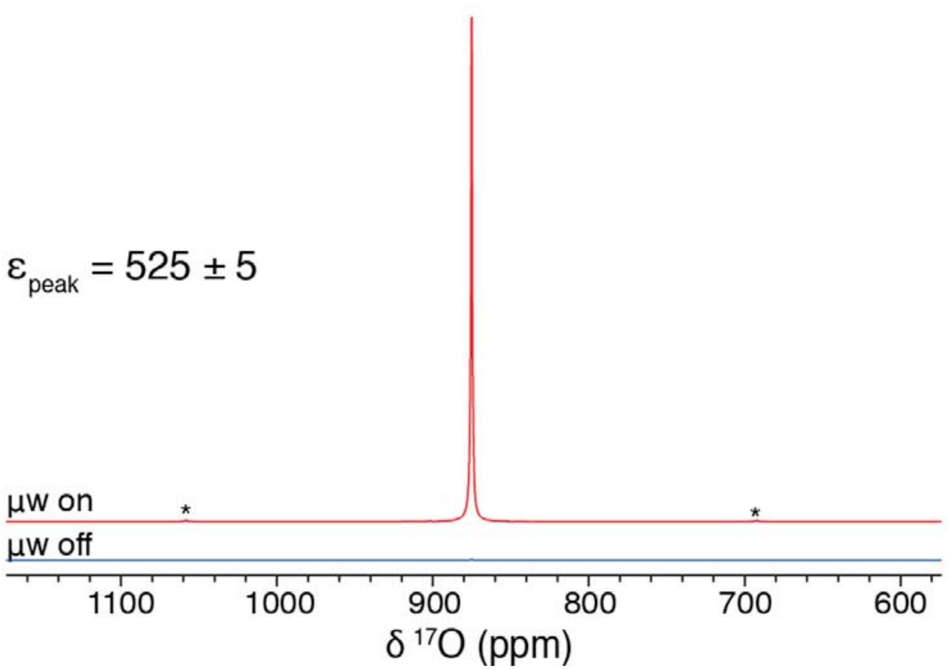
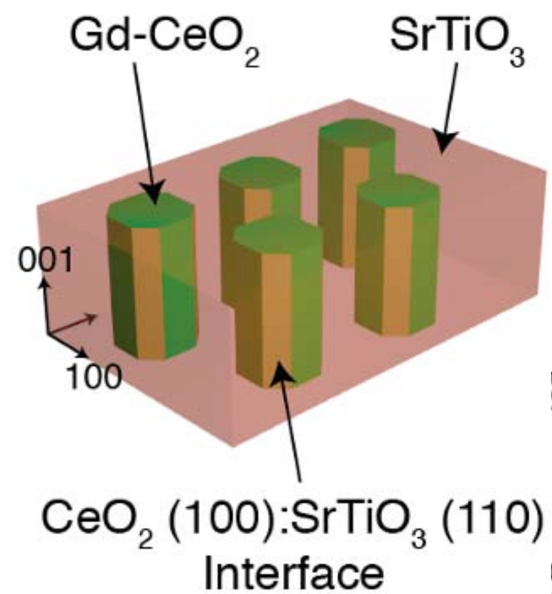
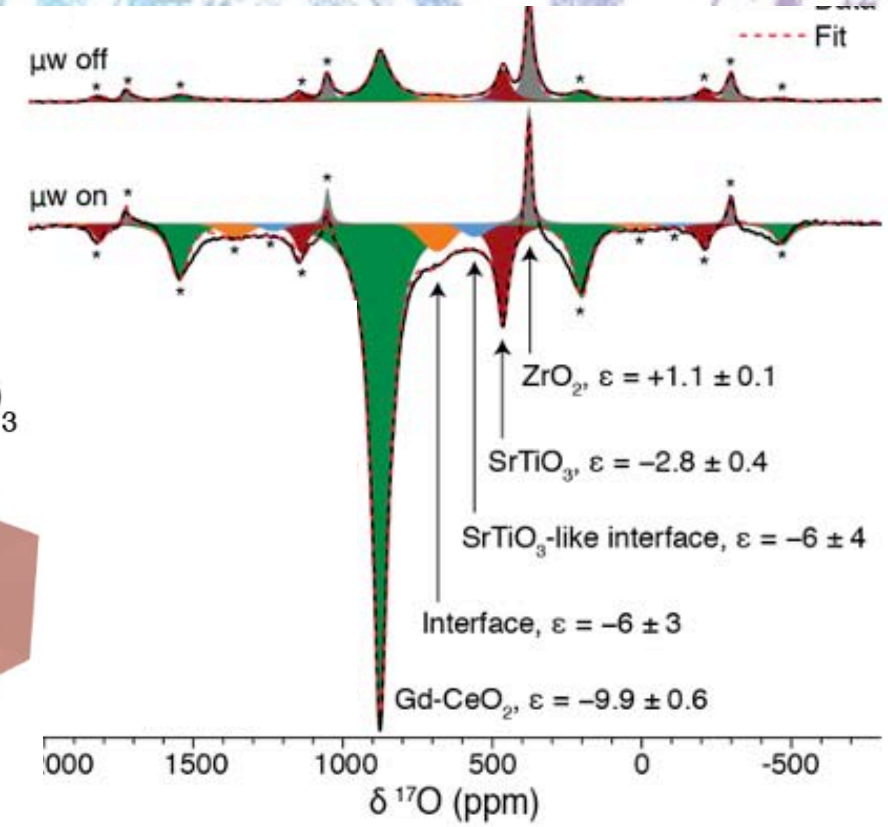
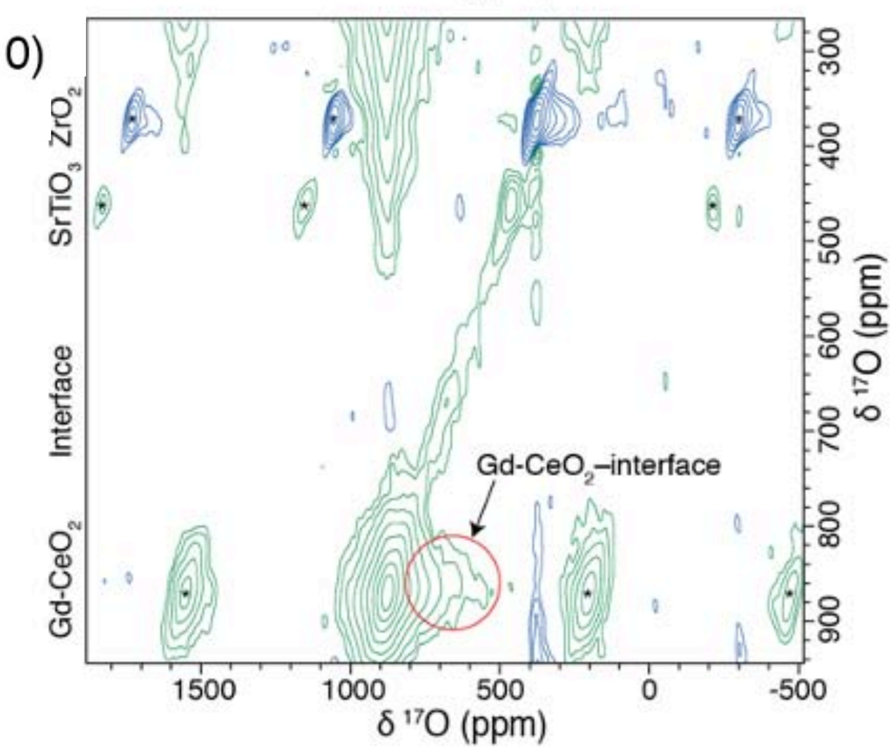




Gd^{3+}-doped CeO_2–$SrTiO_3$







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