# The Role of Formate Mobility for Adaptive Hydrogenation Catalysts Probed by Solid-state NMR Spectroscopy

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## ADAPTIVE HYDROGENATION CATALYSIS
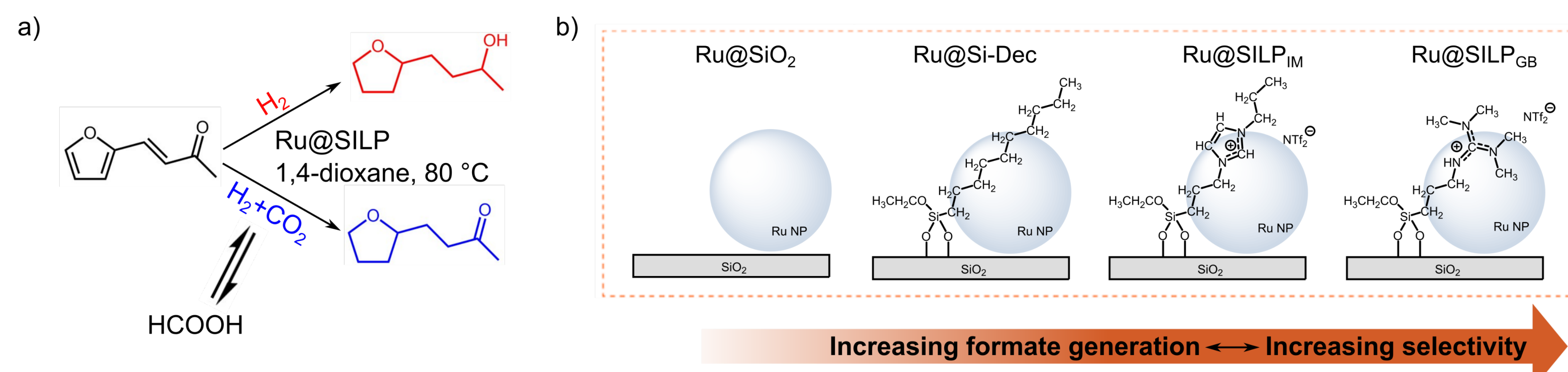


(a) Using **Ru nanoparticle-loaded supported ionic liquid phases (Ru@SILPs)** as **adaptive catalysts** for hydrogenation reactions. When a $H_2/CO_2$ gas mixture is used as feed gas, *in situ*-generated formate inhibits the hydrogenation of the carbonyl groups and thus changes the reaction selectivity.[1] (b) Different hydrogenation catalysts studied in this project. The **$CO_2$-responsive selectivity increases** from left to right accompanied with an **increase in formate concentration** in the reaction mixture.[2]

## COVALENT-BINDING OF IONIC LIQUID TO THE SILICA SURFACE
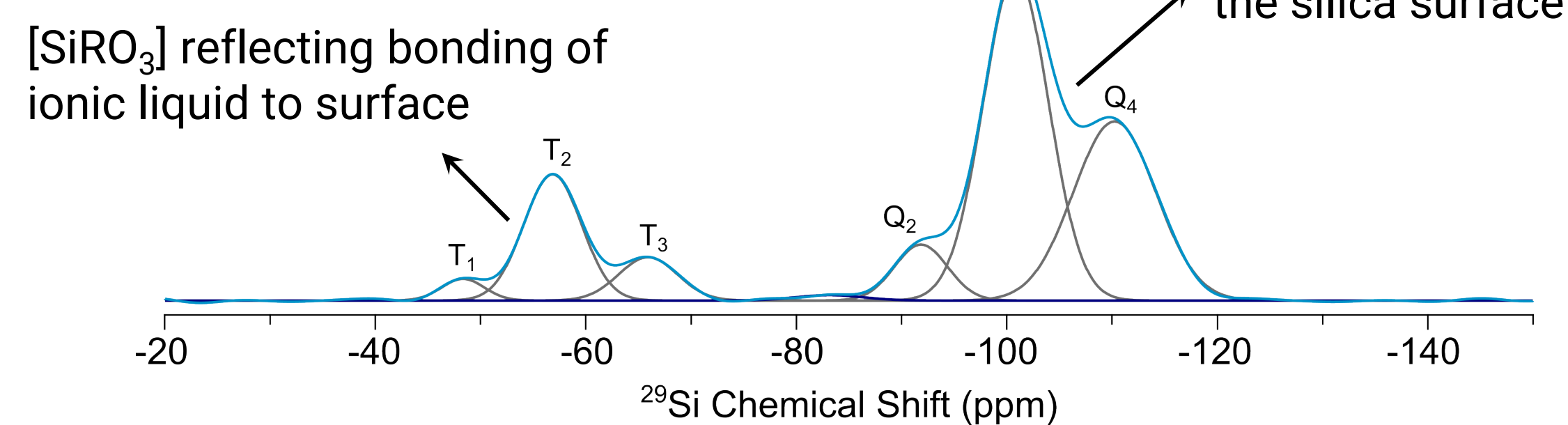


**$^1H$-$^{29}Si$ CP-MAS** spectrum of Ru@SILP$_{GB}$ and line-shape decompositions. $T_{1-3}$ indicate different levels of covalent-grafting. Recorded at 17.0 kHz MAS, 11.7 T.

## IMMOBILIZATION OF FORMATE ON THE SURFACE
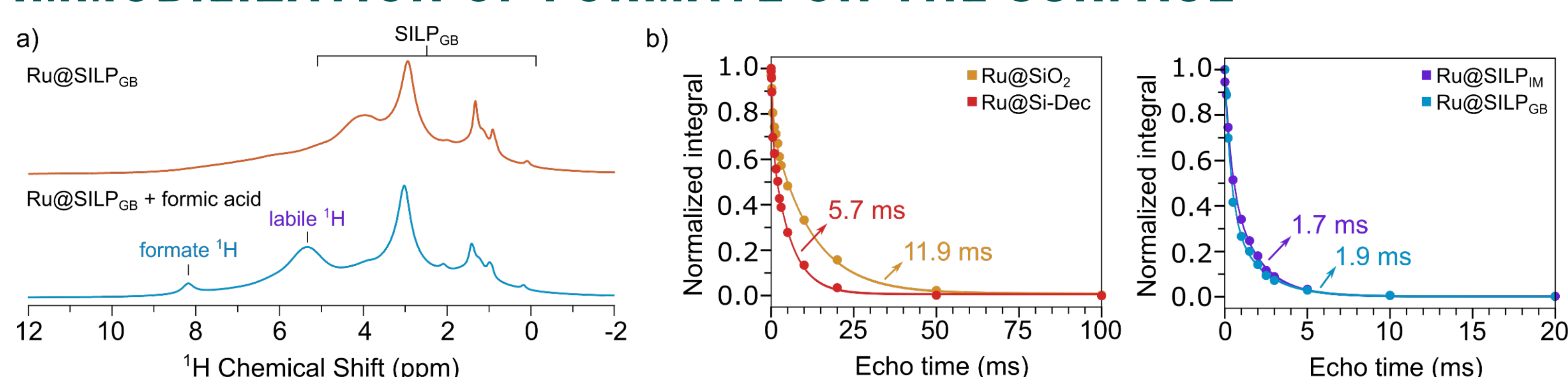


(a) **$^1H$ spin-echo spectra**. The samples were prepared by impregnating formic acid on the catalysts.

(b) $^1H$ transverse relaxation times ($T_2$) of formate determined from spin-echo decay curves as a probe for **molecular mobility**[3]. **Shorter $T_2$-values** on the two SILPs (right) suggest larger residual homonuclear dipolar couplings caused by **immobilization** of formate on the surface. (a-b) Recorded at 17.0 kHz MAS, 11.7 T.
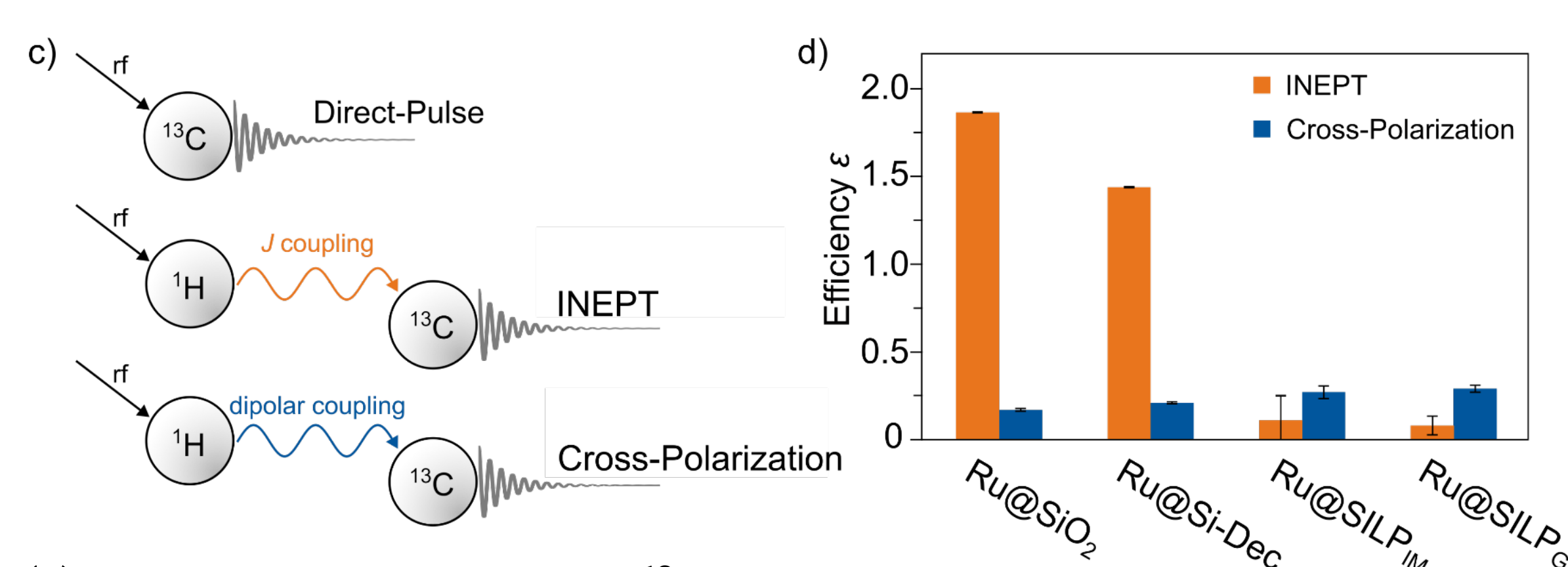


(c) Three techniques to acquire $^{13}C$ MAS NMR spectra.

(d) **Polarization transfer efficiencies** calculated from the ratio of integrals of the formate signal relative to the Direct-Pulse spectra. Formate impregnated on the SILPs showed **low INEPT efficiency and high Cross-Polarization efficiency** suggesting **reduced mobility**.[4] Recorded at 12.0 and 17.0 kHz MAS, 11.7 T.

## INTERACTION BETWEEN FORMATE AND THE SURFACE
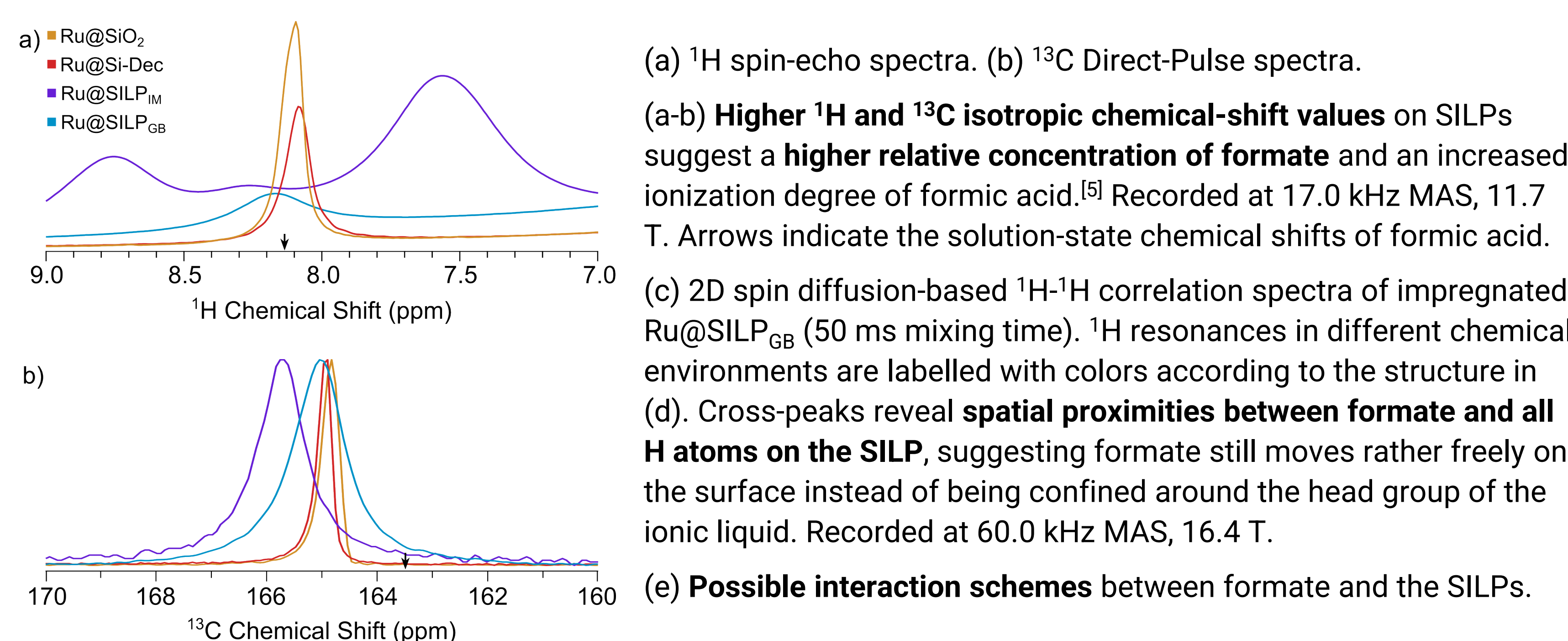


(a) $^1H$ spin-echo spectra. (b) $^{13}C$ Direct-Pulse spectra.

(a-b) **Higher $^1H$ and $^{13}C$ isotropic chemical-shift values** on SILPs suggest a **higher relative concentration of formate** and an increased ionization degree of formic acid.[5] Recorded at 17.0 kHz MAS, 11.7 T. Arrows indicate the solution-state chemical shifts of formic acid.

(c) 2D spin diffusion-based $^1H$-$^1H$ correlation spectra of impregnated Ru@SILP$_{GB}$ (50 ms mixing time). $^1H$ resonances in different chemical environments are labelled with colors according to the structure in (d). Cross-peaks reveal **spatial proximities between formate and all H atoms on the SILP**, suggesting formate still moves rather freely on the surface instead of being confined around the head group of the ionic liquid. Recorded at 60.0 kHz MAS, 16.4 T.

(e) **Possible interaction schemes** between formate and the SILPs.

## DISTANCE MEASUREMENTS FOR DETERMINING SILP CONFORMATIONS AND PROBING ORDERING PHENOMENA
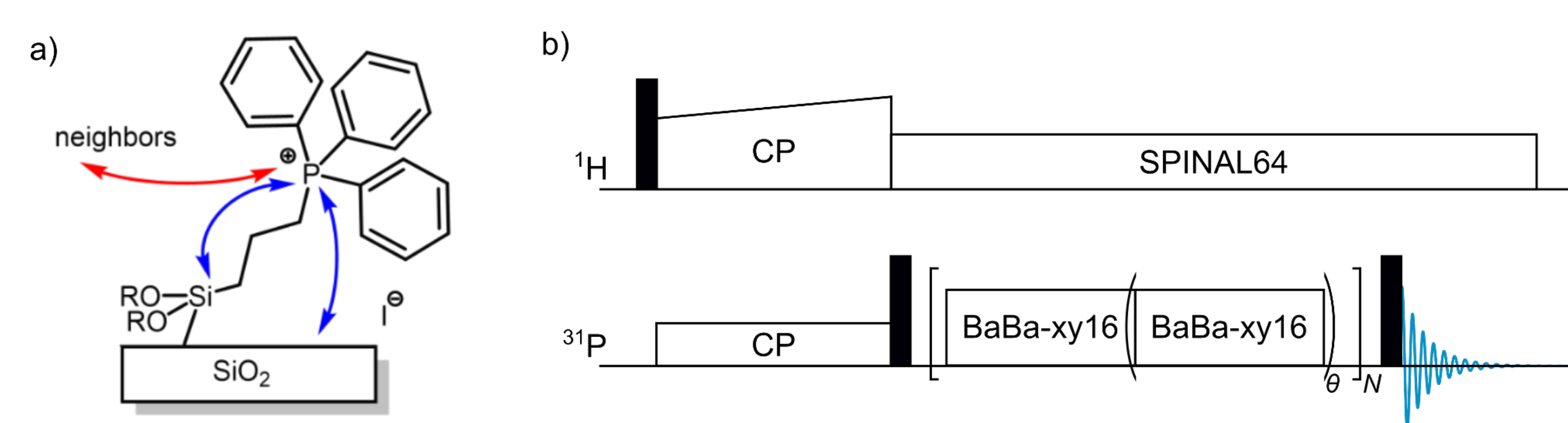


(a) Structure of a **SILP$_{PPh3}$** material as a model system. **$^{31}P$-$^{31}P$ and $^{31}P$-$^{29}Si$ distances** are determined by solid-state NMR experiments to build the conformational model. [6-7] We are currently working on computational modeling of the SILP system based on Molecular Dynamics simulations taking these NMR distances as structural restraints.

(b) Double-Quantum-based Dipolar Re-coupling Effects Nuclear Alignment Reduction (**DQ-DRENAR**) experiment for measuring **homonuclear dipolar coupling** strengths between $^{31}P$ spins.[8] The relative differences of the signal with ($S'$, phase shift $\theta$=0) and without dipolar-recoupling ($S_0$, phase shift $\theta$=90°) are fitted as a function of the re-coupling time $NT_r$.
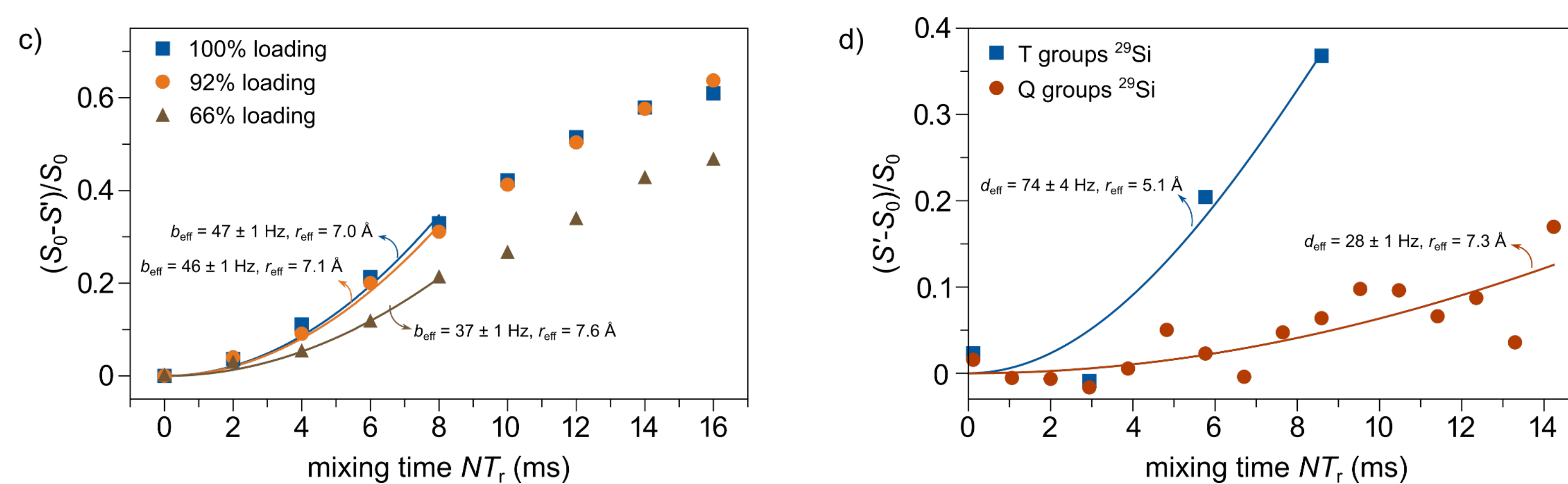
(c) Result of the $^{31}P$ DQ-DRENAR experiments measured on SILP$_{PPh3}$ materials with different loading degrees. First five data points were fitted to a quadratic function $(S_0-S')/S_0 = 0.86\pi^2(b_{eff}NT_r)^2/15$ to extract the **$^{31}P$-$^{31}P$ effective dipolar coupling strengths and distances**. Reduction in the distances at lower loading degrees suggests a change in the grafting density instead of the coverage area. Spectra recorded at 200 K, 8.0 kHz MAS, 11.7 T. Loading degrees are relative to the highest one.

(d) Result of the $^{29}Si\{^{31}P\}$ REDOR experiments measured on the SILP$_{PPh3}$ material with the highest loading degree. Spectra recorded at 280 K, 17.0 kHz MAS, 16.4 T.

## CONCLUSIONS

- $^1H$ $T_2$ and $^{13}C$-detected experiments proved the immobilization effect of formate on SILPs.
- $^1H$ and $^{13}C$ chemical-shift values and the $^1H$-$^1H$ spin-diffusion spectrum provide information about the molecular interactions involving the positively charged head groups on the ionic liquid.
- Interactions identified by NMR confirm the previously observed increasing formic acid generation.
- $^{31}P$-$^{31}P$ and $^{31}P$-$^{29}Si$ effective dipolar coupling strengths and distances were measured with solid-state NMR experiments, which can be used to study the structure and conformation of SILPs.

## REFERENCES

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