

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



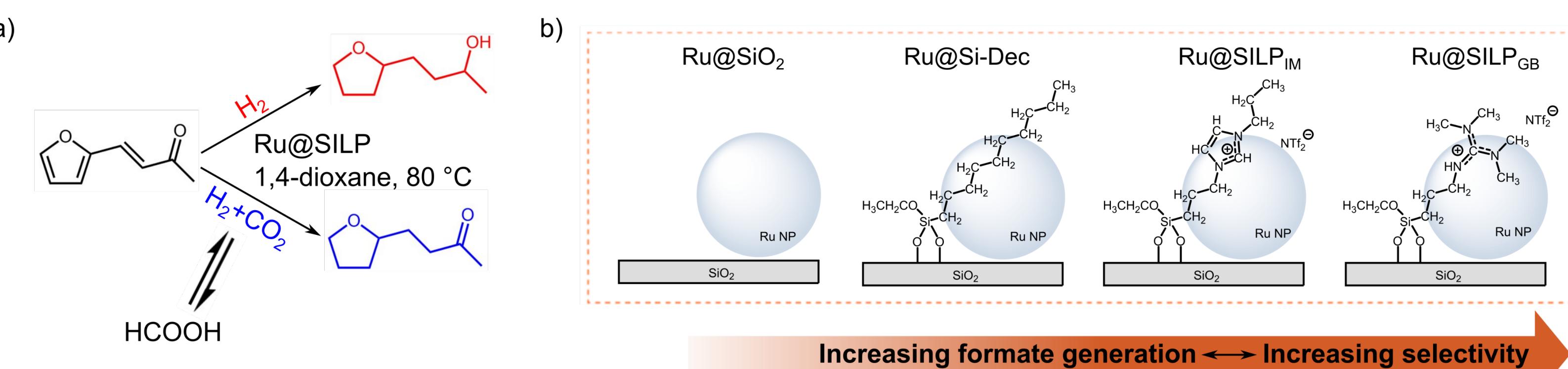
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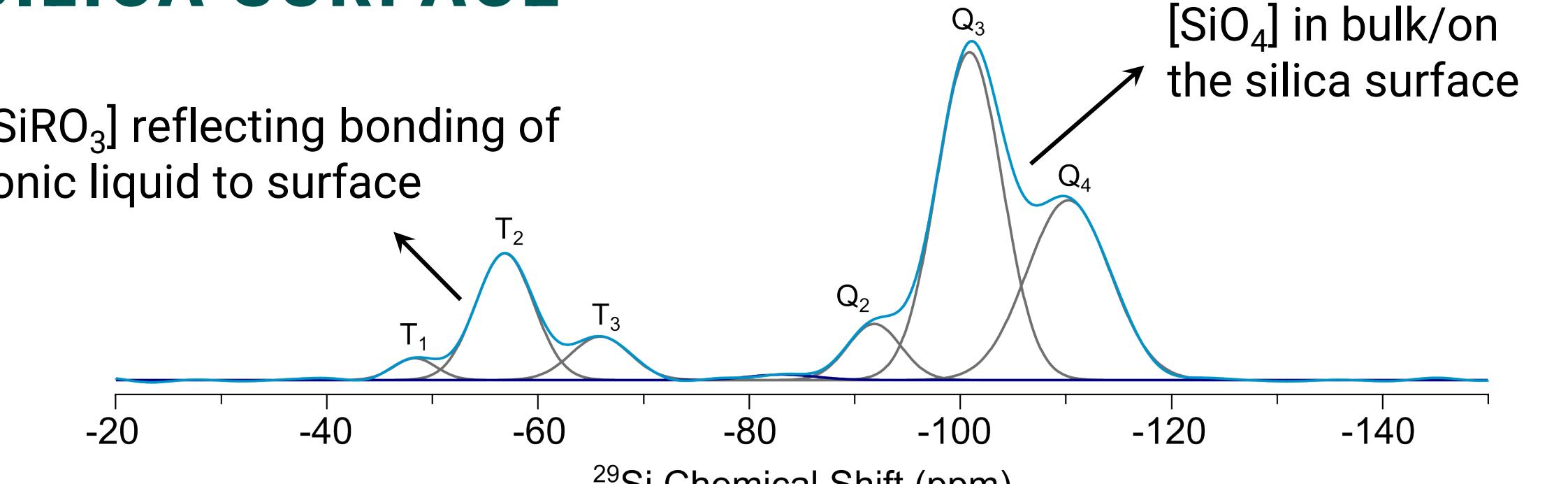
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ADAPTIVE HYDROGENATION CATALYSIS

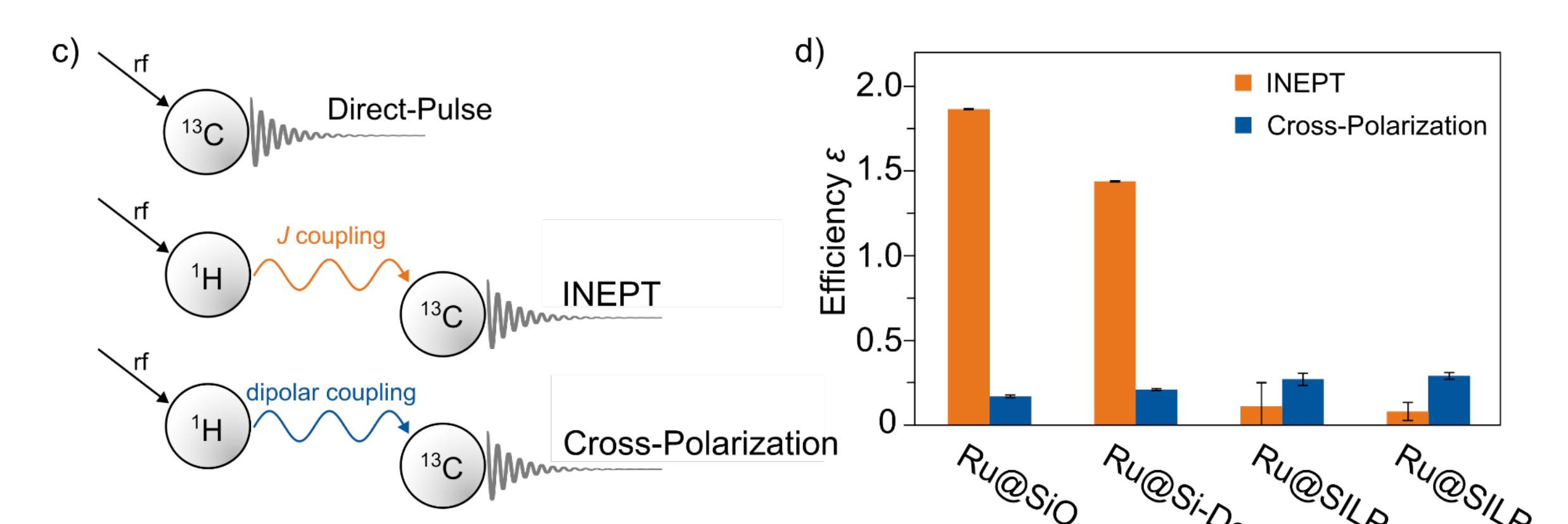
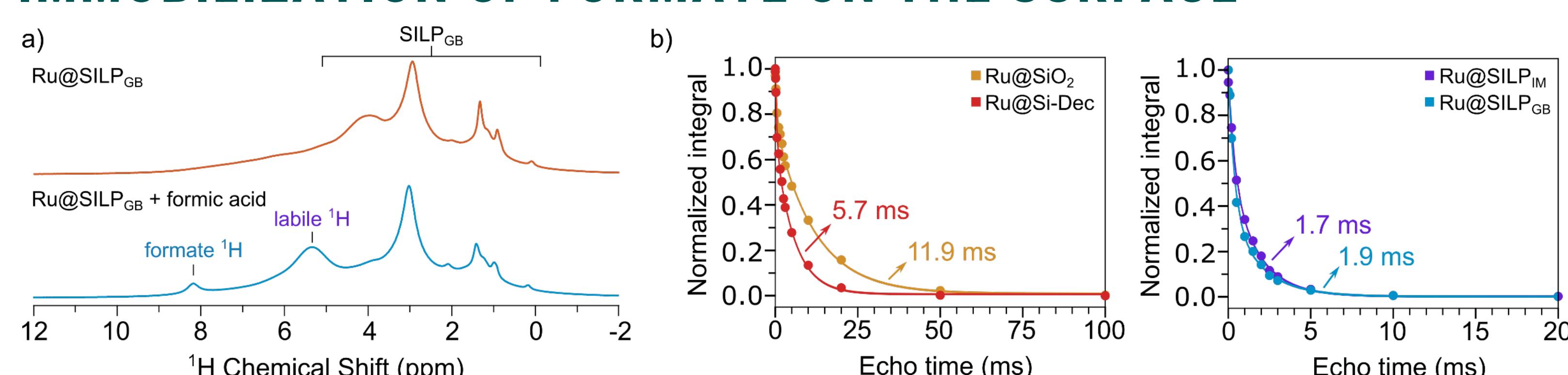


(a) Using Ru nanoparticle-loaded supported ionic liquid phases (Ru@SILPs) as adaptive catalysts for hydrogenation reactions. When a H₂/CO₂ gas mixture is used as feed gas, *in situ*-generated formate inhibits the hydrogenation of the carbonyl groups and thus changes the reaction selectivity.^[1] (b) Different hydrogenation catalysts studied in this project. The CO₂-responsive selectivity increases from left to right accompanied with an increase in formate concentration in the reaction mixture.^[2]

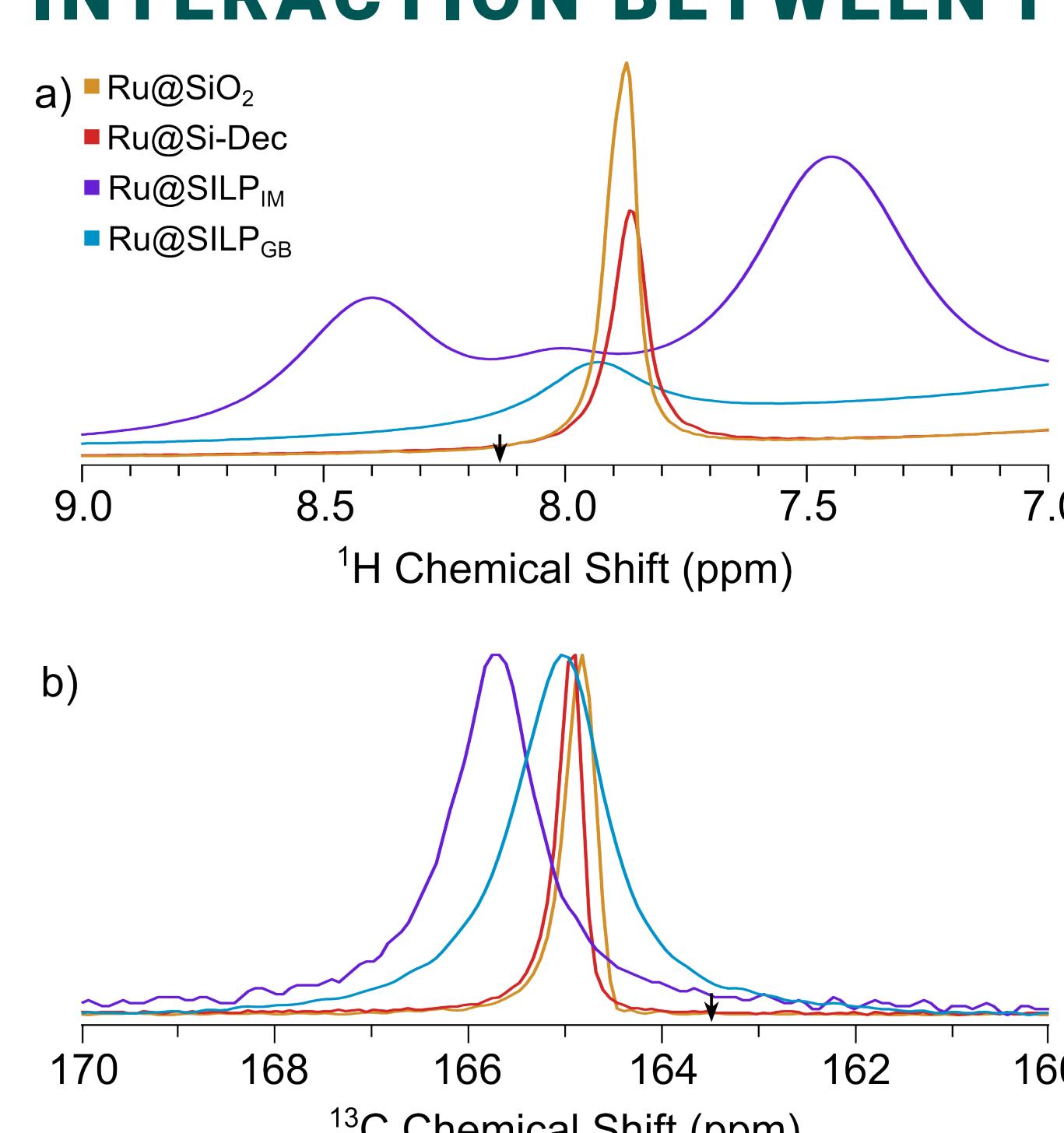
COVALENT-BINDING OF IONIC LIQUID TO THE SILICA SURFACE



IMMOBILIZATION OF FORMATE ON THE SURFACE

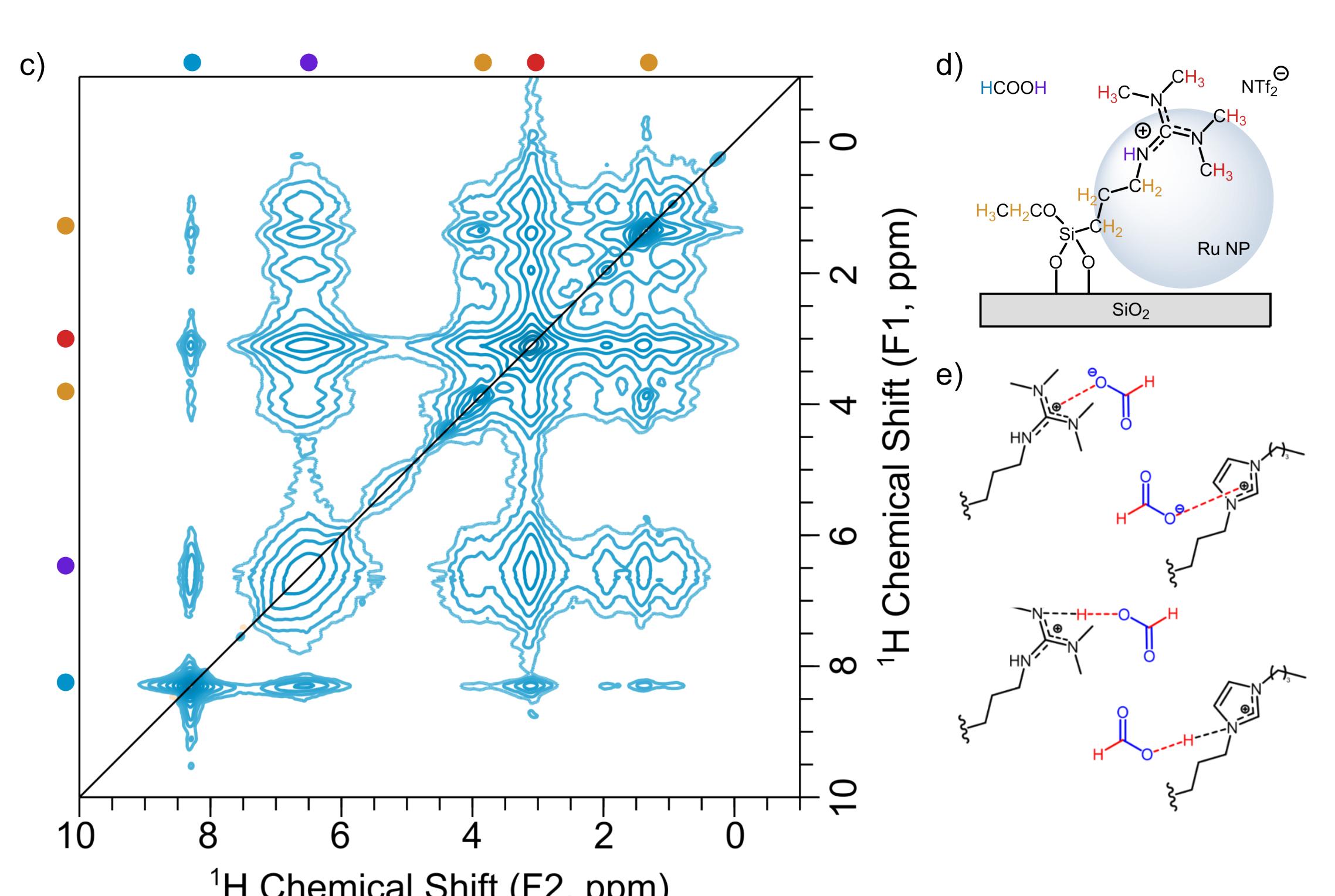


INTERACTION BETWEEN FORMATE AND THE SURFACE

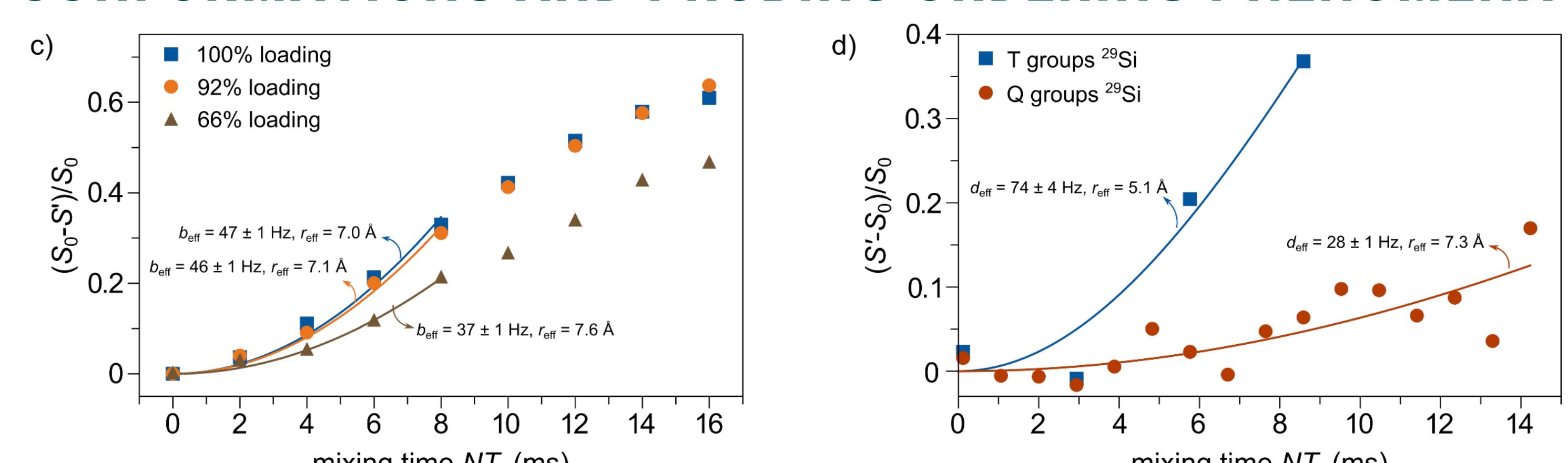
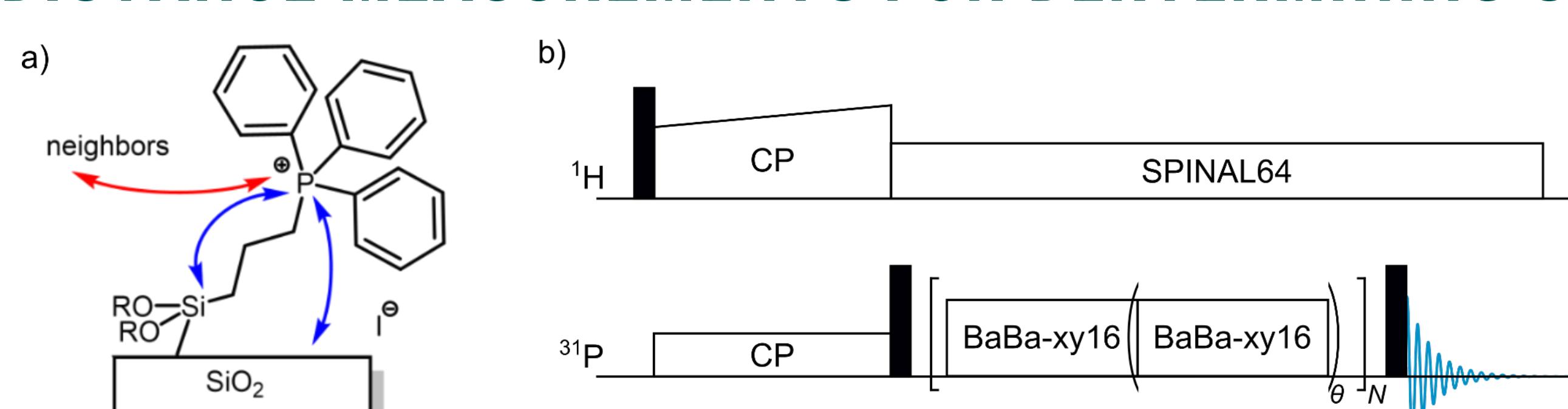


(a-b) Higher ¹H and ¹³C isotropic chemical-shift values on SILPs suggest a higher relative concentration of formate and an increased ionization degree of formic acid.^[5] Recorded at 17.0 kHz MAS, 11.7 T. Arrows indicate the solution-state chemical shifts of formic acid. (c) 2D spin diffusion-based ¹H-¹H 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



CONCLUSIONS

- ¹H T₂ and ¹³C-detected experiments proved the immobilization effect of formate on SILPs.
- ¹H and ¹³C 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.
- ³¹P-³¹P and ³¹P-²⁹Si 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.

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