



Development of Silica-Based Resins for Lanthanide Separation

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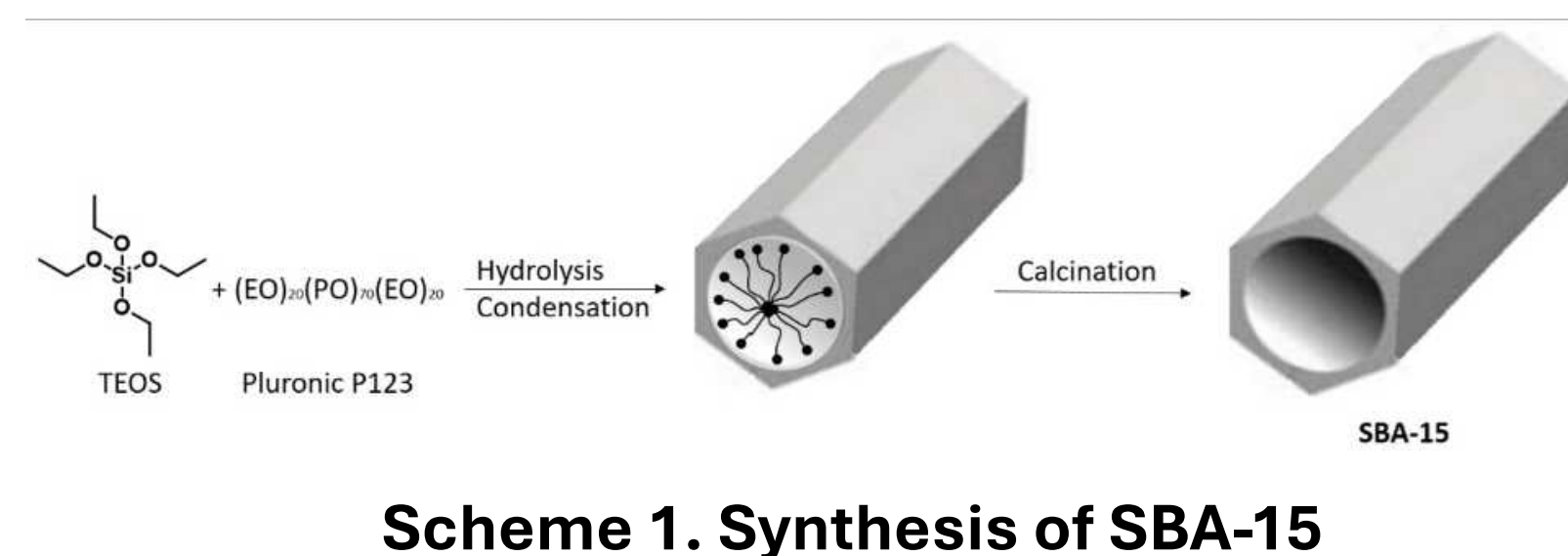
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Introduction

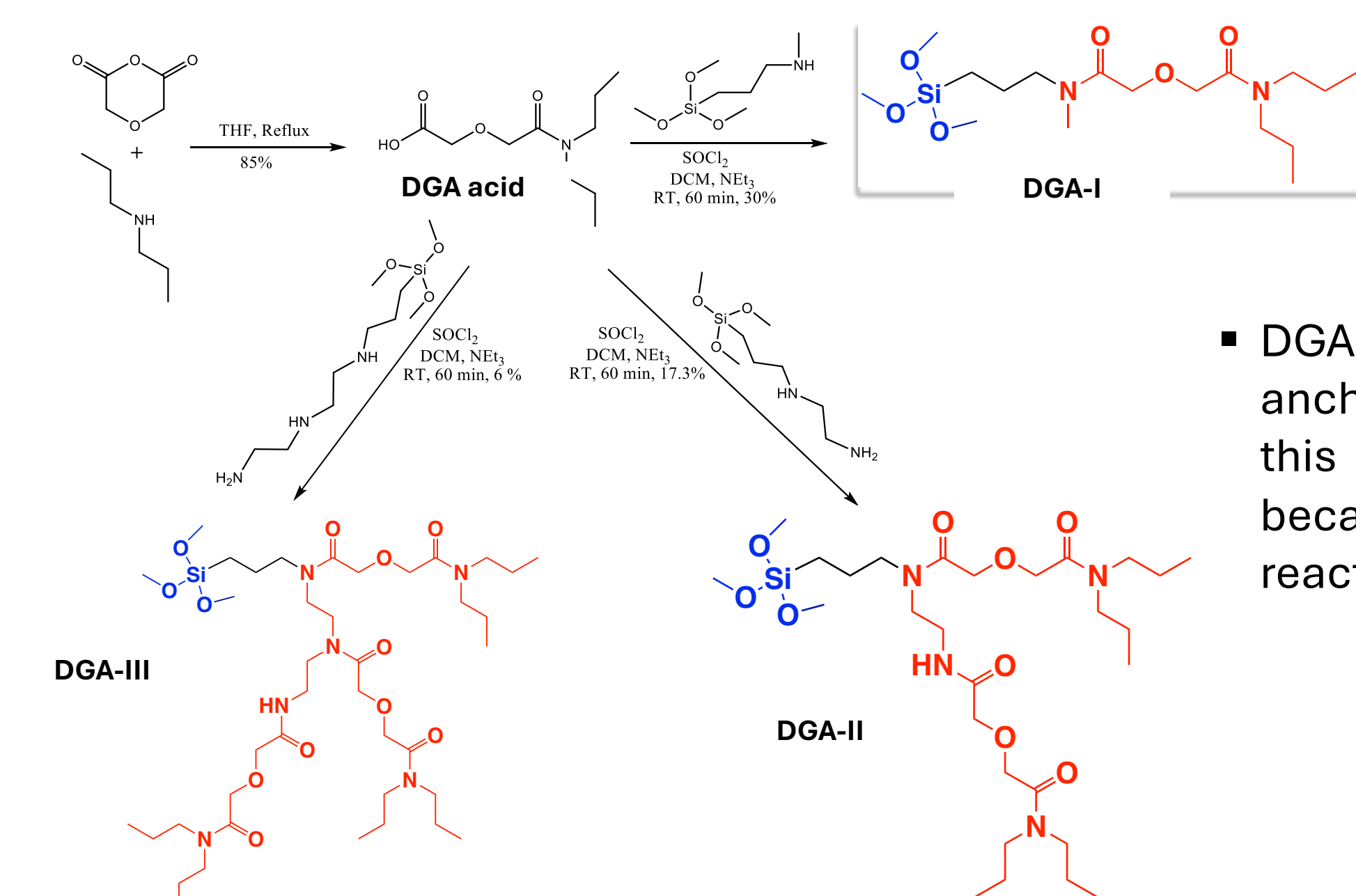
Separating trivalent lanthanides and actinides is challenging due to their similar chemical properties, complicating efficient extraction and purification for medical applications. Current methods often rely on liquid-liquid extraction, generating significant toxic organic waste. This study focuses on using diglycolamide (DGA) ligands, known for their exceptional radiation and acid resistance, and mesoporous silica (SBA-15) as a solid support. The separation of trivalent lanthanides is important in many fields, especially medical isotopes. For the purpose of this study, it aims to be applied in targeted radionuclide therapy. Specifically, therapeutic radionuclides such as ¹⁶¹Tb, ¹⁶⁵Er, and ¹⁷⁷Lu have shown great promise in treating cancer and other diseases. The research involves covalently bonding DGA ligands to SBA-15 to enhance stability and efficiency. Additionally, the prearrangement of DGA ligands on the surface is explored to improve binding accessibility and maximize ligand utilization during the extraction process.

Synthesis of Materials

- The synthesis of the mesoporous silica (SBA-15) used Tetraethyl-orthosilicate (TEOS) as the precursor to introduce silicon and Pluronic P123 as the triblock copolymer surfactant.



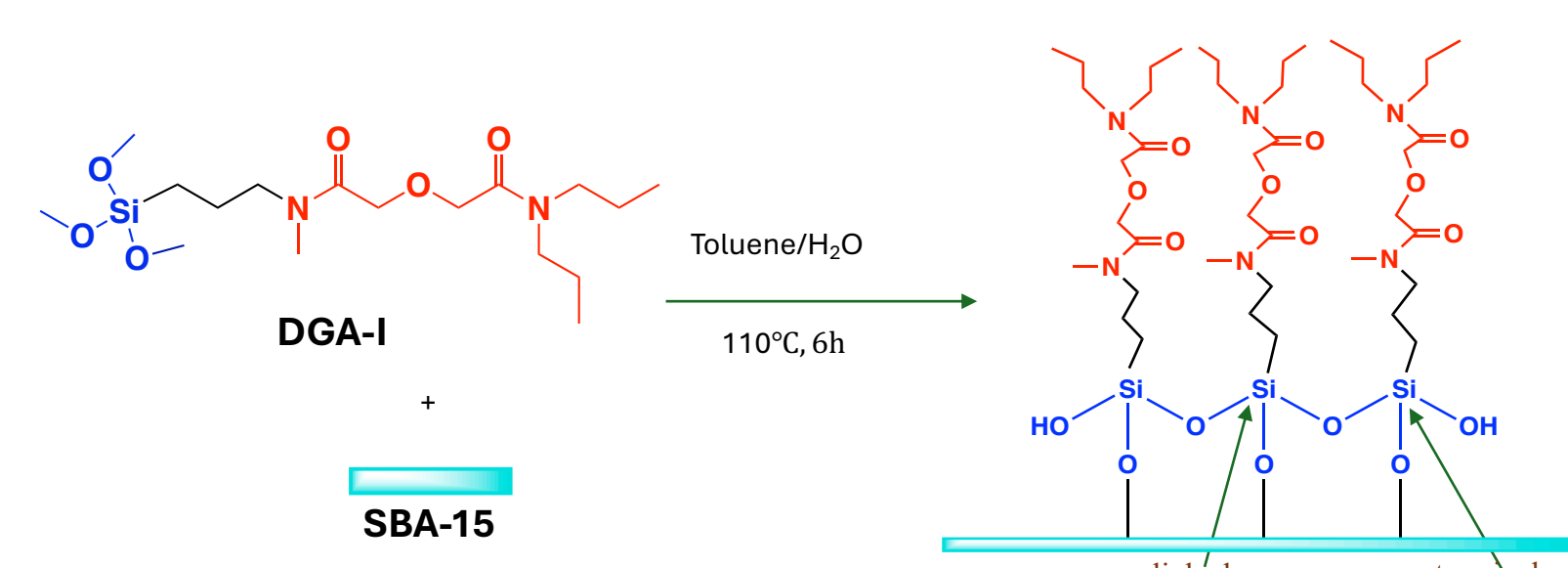
Scheme 1. Synthesis of SBA-15



Scheme 2. Synthesis of DGA-I, DGA-II and DGA-III

- Scheme 3 is the same scheme used to synthesize SBA-DGA-II and SBA-DGA-III
- Grafting technique was used to immobilize the extractant ligand on the solid support.

- SBA-DGAs were tested for acid stability in 1M HNO₃ for 24 hours and contacted with Eu³⁺



Scheme 3. Synthesis of SBA-DGA-I

Results

A. SBA-15 Characterization

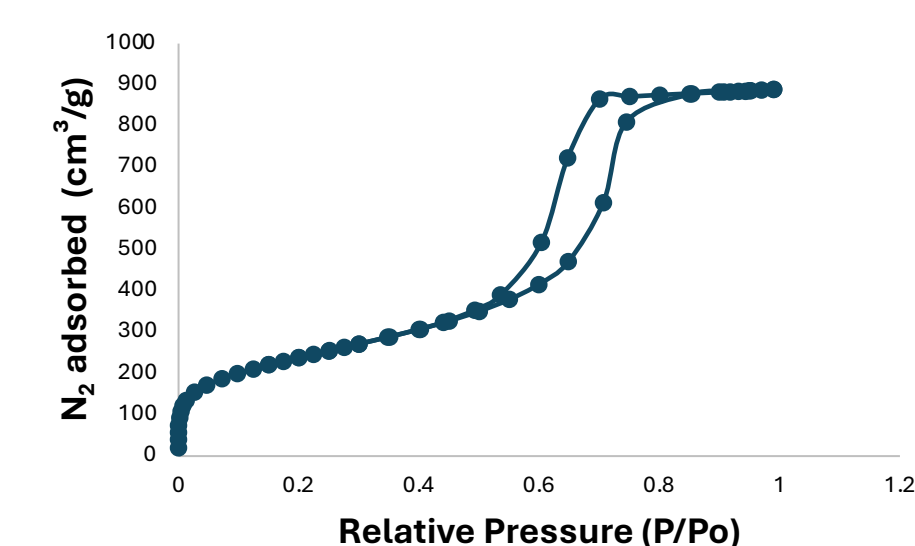


Figure 1. Nitrogen adsorption/desorption isotherms of SBA-15

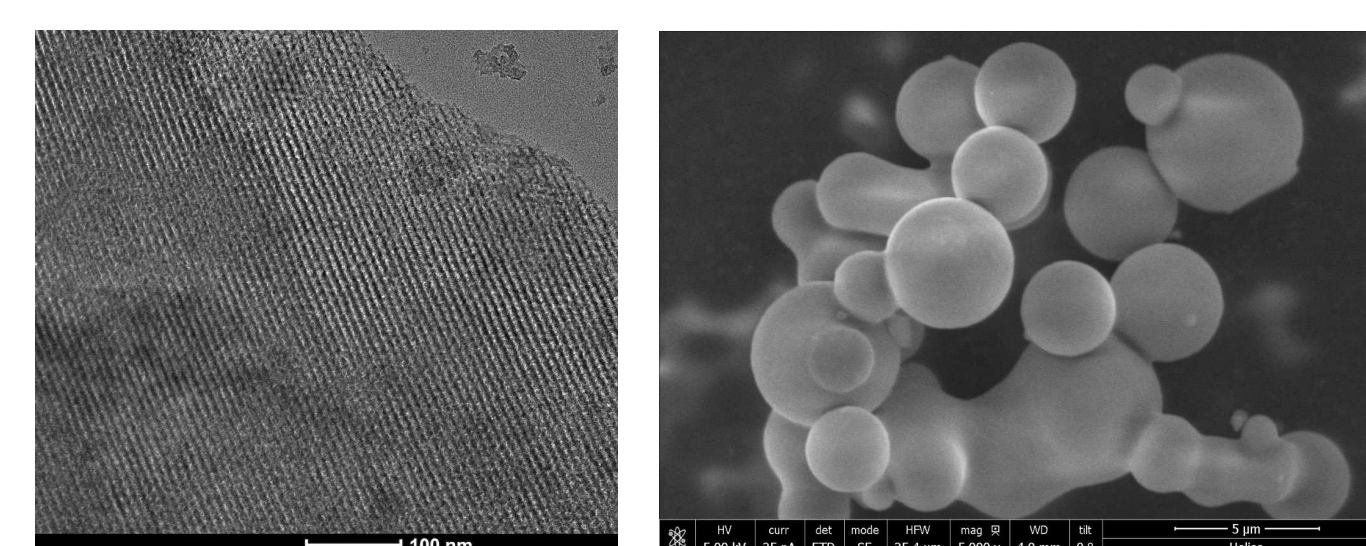


Figure 2. TEM (left) and SEM (right) of SBA-15
SBA-15 surface area: 807 m²/g

B. Acid Stability and Sorption Capacity Studies

Table 1. N₂ adsorption analysis of SBA-15 and SBA-DGAs.

Material	BET surface area ^a , m²/g	Pore diameter ^b , nm
SBA-15	807	7.78
SBA-DGA-I (p ^b)	301	6.30
SBA-DGA-I (ac ^c)	298	6.35
SBA-DGA-II (p ^b)	232	4.29
SBA-DGA-II (ac ^c)	249	4.34
SBA-DGA-III (p ^b)	302	5.39
SBA-DGA-III (ac ^c)	317	5.66

a – Based on the N₂ physisorption analysis
b – p for pristine resin
c – ac for acid-contacted resin

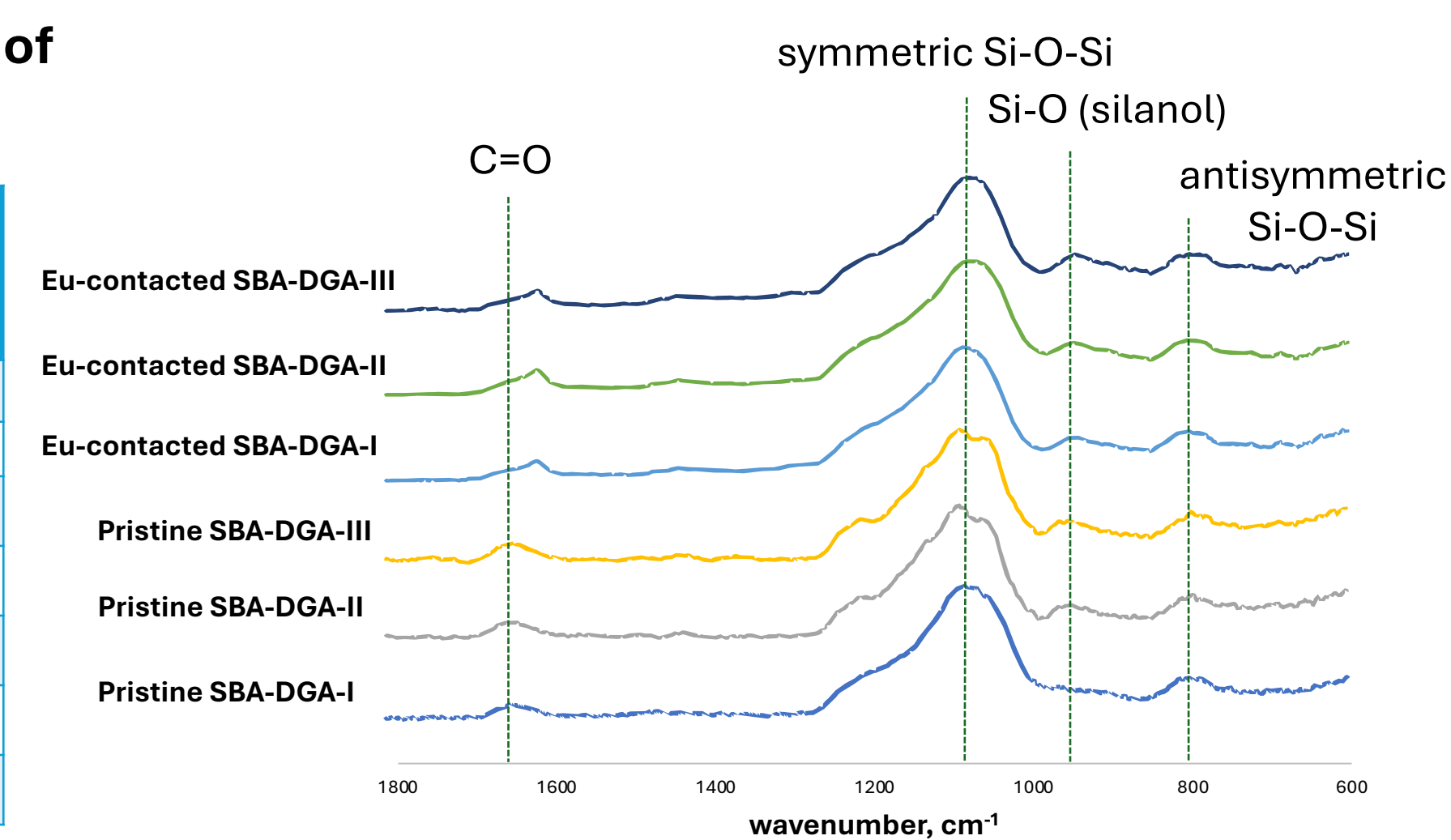


Figure 3. IR spectra of pristine & Eu-contacted SBA-DGAs

- Additional peak for SBA-DGAs → amide carbonyl peak (1640 cm⁻¹)
- Eu-contacted materials → C=O peak shifts to 1628 cm⁻¹ indicates that the Eu is coordinating through the carbonyls

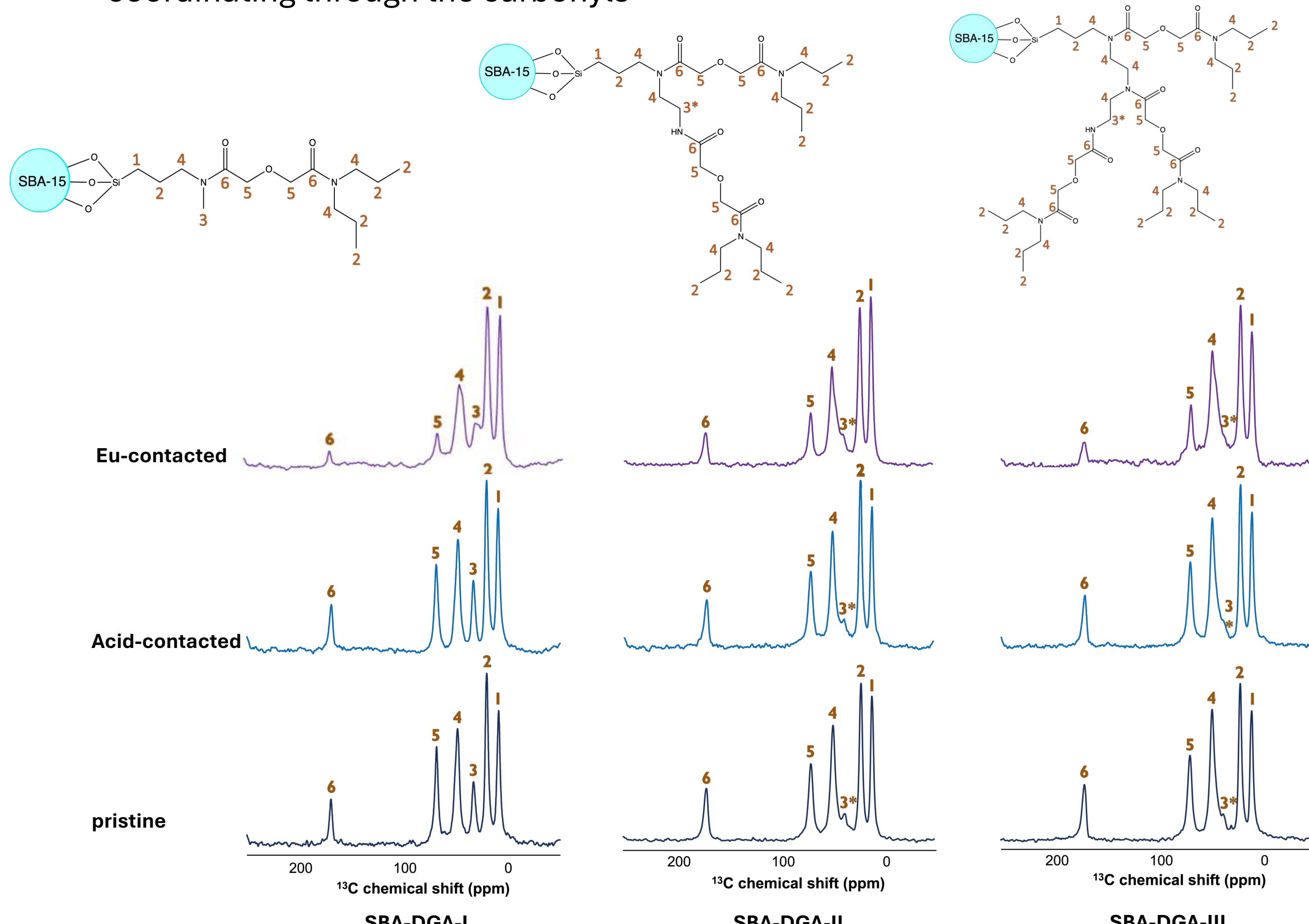


Figure 4. ¹³C{¹H} CP/MAS NMR spectra of pristine, acid- and Eu-contacted SBA-DGAs

- A difference in peak #3 is observed → SBA-DGA-I, this carbon is adjacent to a tertiary amide whereas this carbon is a secondary amide for SBA-DGA-II and SBA-DGA-III
- A significant decrease at peaks #3-5 for Eu-contacted materials because of Eu's paramagnetism → these carbons are the closest to the binding site

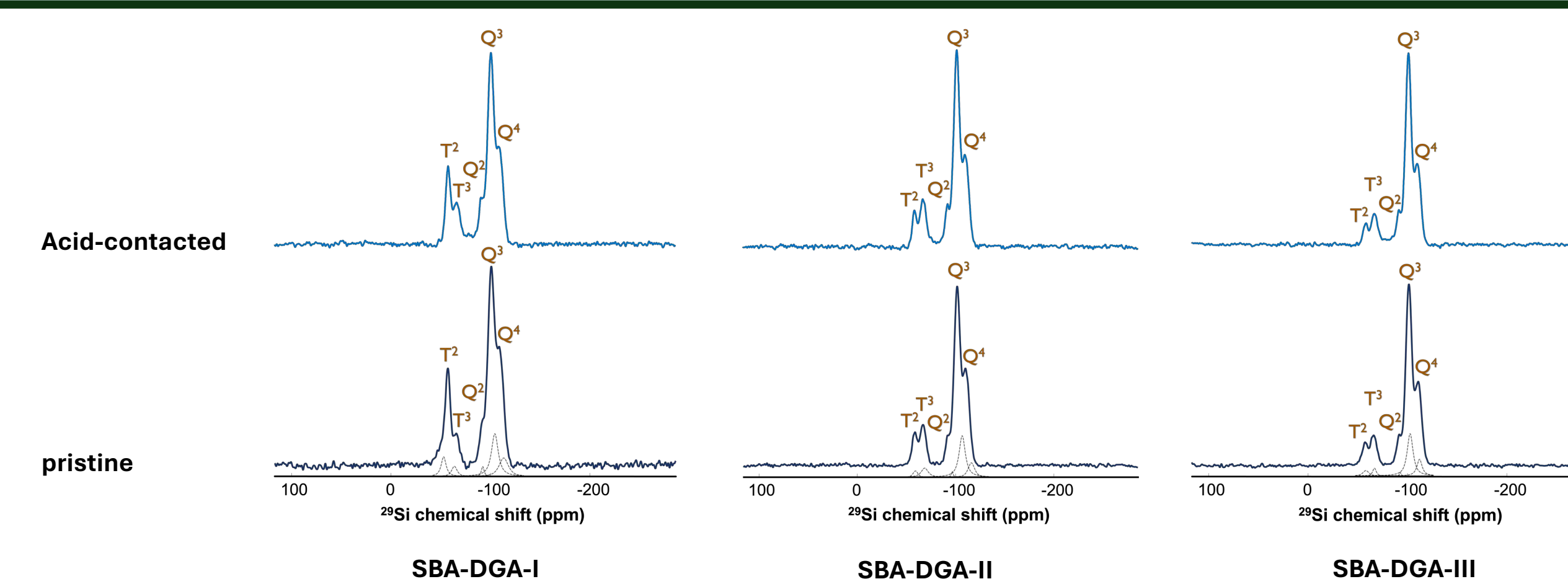


Figure 5. ²⁹Si{¹H} CP/MAS NMR spectra of pristine and acid-contacted SBA-DGAs

- The presence of only T² and T³ peaks indicates high order ligand polymerization
- T and Q peak ratios show close similarity → acid contact did not degrade the materials

Table 2. Data on the sorption capacity of the SBA-DGA resins.

Material	Sorption capacity	Ligand density (ac), silanes per nm²	Ligand loading (ac), μmol/g	Ligand-to-metal ratio
SBA-DGA- I	500.0 μmol/g (75.2 mg Eu/g resin)*	0.91	1218	2.4
SBA-DGA- II	476.2 μmol/g (73.5 mg Eu/g resin)	0.55	731	1.5
SBA-DGA- III	476.2 μmol/g (73.5 mg Eu/g resin)	0.37	500	1.0

*Versus 203 μmol/g (commercially available) and other previously reported Eu capacity with analogous DGA resins

Conclusion

The study on silica-based resins for lanthanide separation revealed that SBA-DGA materials exhibit significant acid stability in 1M HNO₃, with solid-state NMR confirming binding of Eu(III) to the DGA ligand. Notably, SBA-DGA-I demonstrated the highest sorption capacity due to its high ligand density and ligand-to-metal ratio compared to the other variants. These results highlight the potential of SBA-DGA materials for efficient lanthanide separation, setting the stage for future research on their application with other lanthanides and in column studies.

References

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