

# An Investigation of the Influence of Polycyclic Aromatic Groups on the Structure and Properties of Polysilsesquioxane Melting Gels

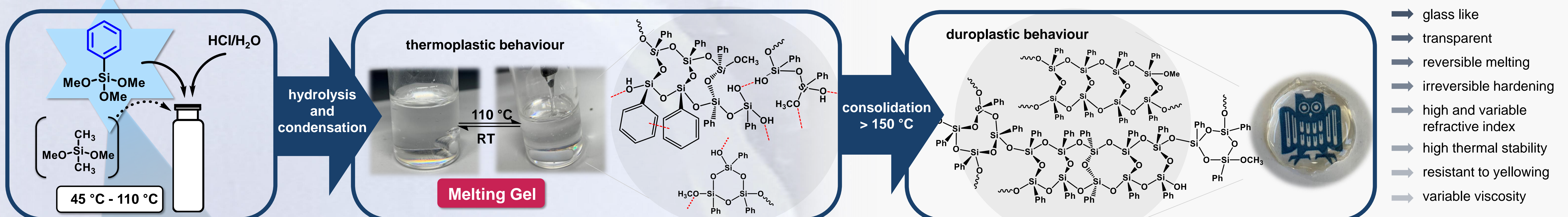
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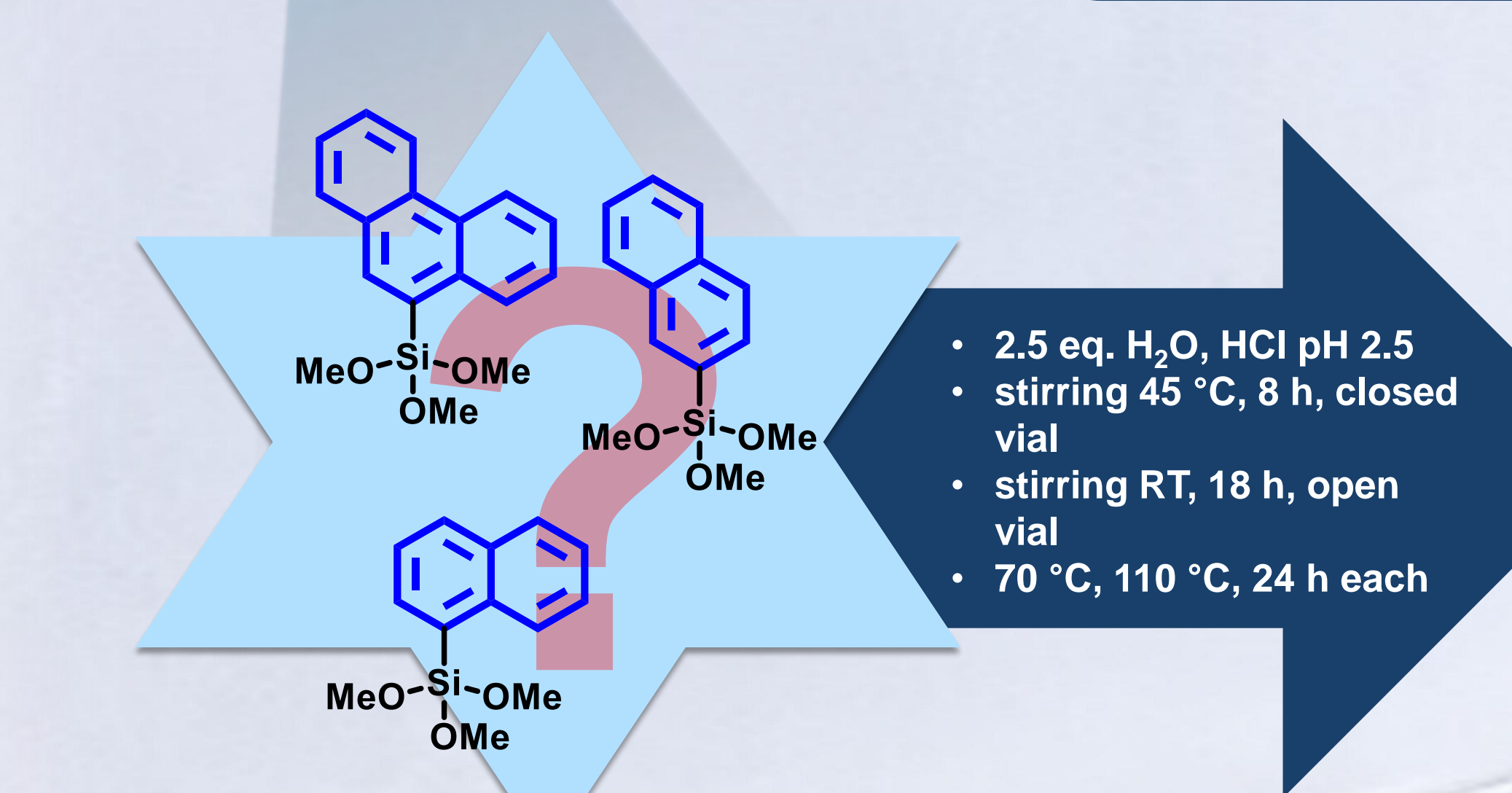


## Introduction

Polysiloxanes, produced by combined hydrolysis and condensation reaction of di- and trialkoxysilanes with methyl or phenyl groups build so-called melting gels (MG).<sup>1</sup> They are rigid and transparent at room temperature, soften reversibly around 110 °C, and show irreversible curing above 150 °C. The glassy, transparent, and insoluble materials show extraordinary properties, like high transparency over a wide range of wavelengths and high thermal stability. A variable refractive index and adjustable viscosity of the precursor gel make the material interesting for many applications, especially in the optoelectronic field.<sup>2</sup> The investigation of the acid-catalyzed solvent-free melting gel formation by various spectroscopic techniques, X-ray diffraction, thermal analysis, and chromatographic methods of a polyphenylsilsesquioxane (Ph-MG) show a defect rich structure with ladder-like domains.  $\pi$ - $\pi$ -Interactions and hydrogen bonding initially cause the thermoplastic behaviour of the precursor gel. Condensation reactions initiated by higher temperatures lead to structural reorientation and irreversible curing.<sup>3</sup> Based on these results we investigated the influence of further aryl compounds like 1-naphthyl-, 2-naphthyl and phenanthrenyltrimethoxysilane on the melting gel formation. We studied the influence of steric hindrance and mode of aromatic group bonding on the crosslinking, the resulting structures, and the OH-group stability to gain an understanding of the structural features and their impact on the melting gel properties.



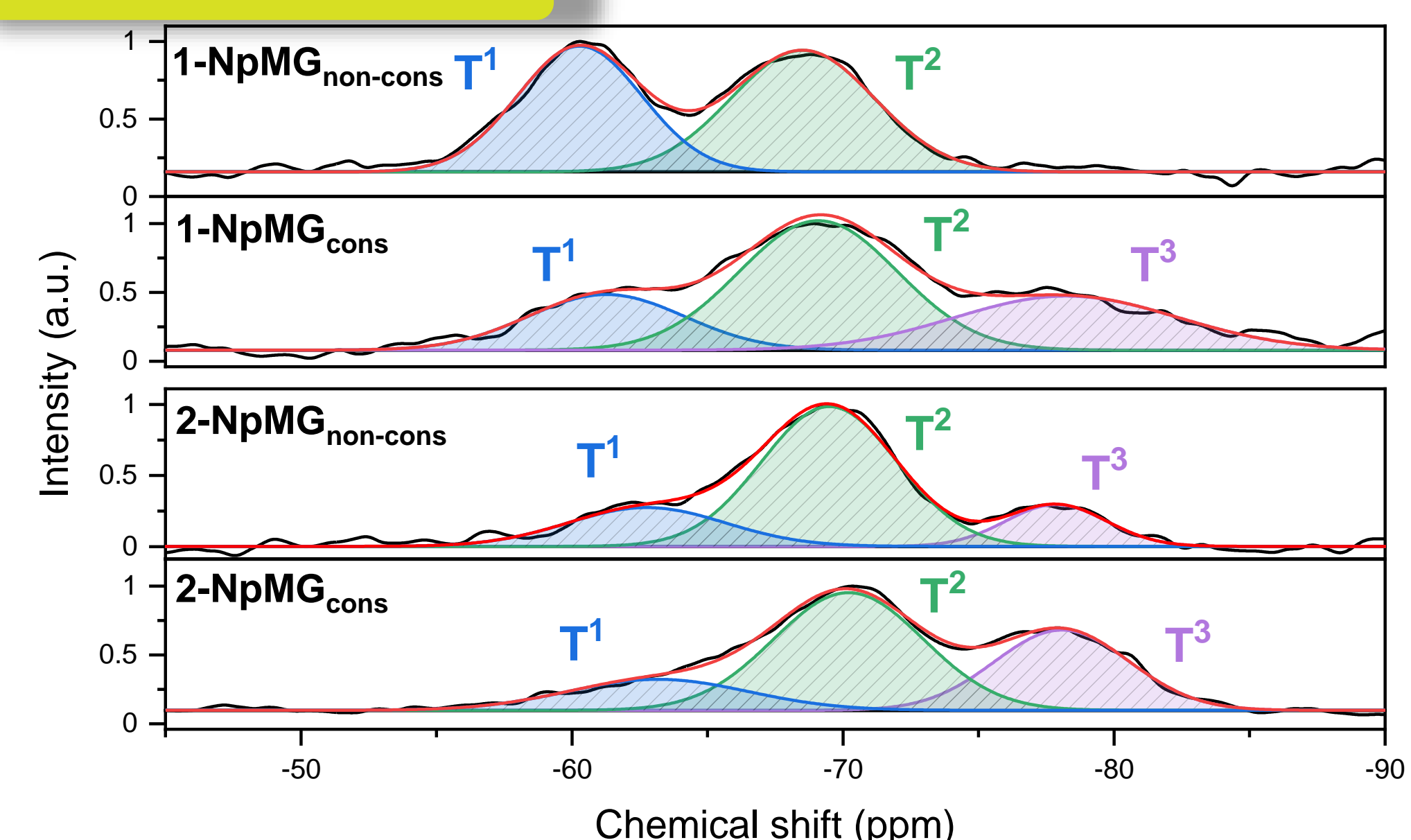
- glass like
- transparent
- reversible melting
- irreversible hardening
- high and variable refractive index
- high thermal stability
- resistant to yellowing
- variable viscosity



Melting Gel	Ph	1-Np	2-Np
glass like	✓	✓	✓
reversible softening at 110 °C <sup>a</sup>	✓	✓	✓
transparent	✓	✓	✓
irreversible curing at 200 °C <sup>b</sup>	✓	✗	✓ <sup>c</sup>
resistant to yellowing	✓	✗	✗
insoluble after consolidation	✓	✗	✓
T <sub>g</sub> [°C] (non-cons/cons)	59/✗	42/63	53/✗

<sup>a</sup>determined by DSC-measurements  
<sup>b</sup>no deformation under pressure at 200 °C  
<sup>c</sup>building of bubbles

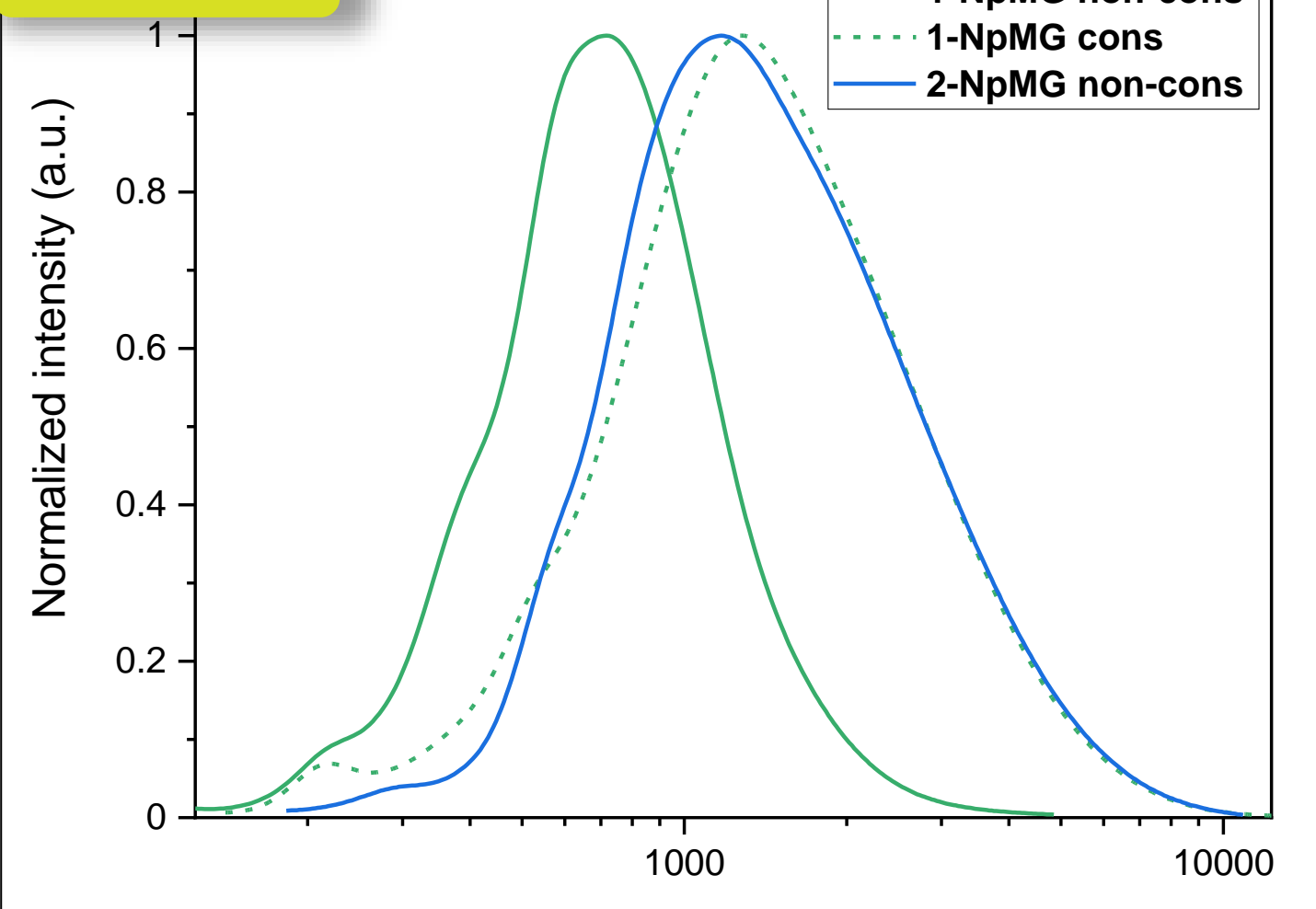
## <sup>29</sup>Si MAS-NMR



Chemical shift [ppm]	T <sup>1</sup> [%]	T <sup>2</sup> [%]	T <sup>3</sup> [%]	DC [%]
-60...-63	47	53	/	51
-68...-70	29	50	21	64
-77...-78	19	60	21	67
	16	52	32	72

- no more monomer
- DC(1-NpMG) < DC(2-NpMG) → 2-NpSi(OMe)<sub>3</sub> higher hydrolysis and condensation rate
- consolidation = further condensation reactions → higher crosslinking

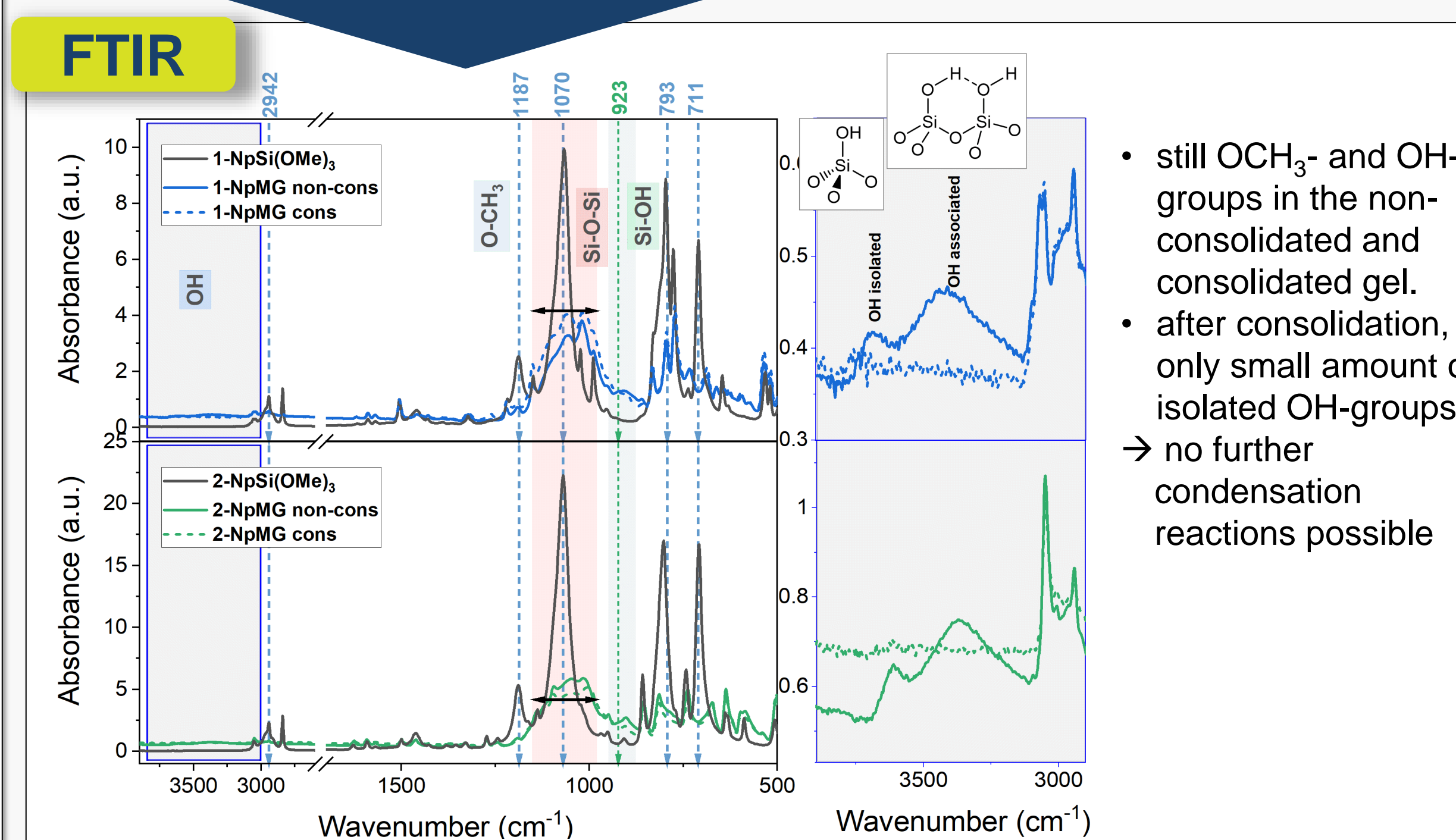
## SEC



	M <sub>n</sub> [g/mol]	M <sub>w</sub> [g/mol]	D
1-NpMG non-cons	618	737	1.19
1-NpMG cons	1314	2139	1.63
2-NpMG non-cons	1165	1709	1.46
2-NpMG cons	Not soluble		

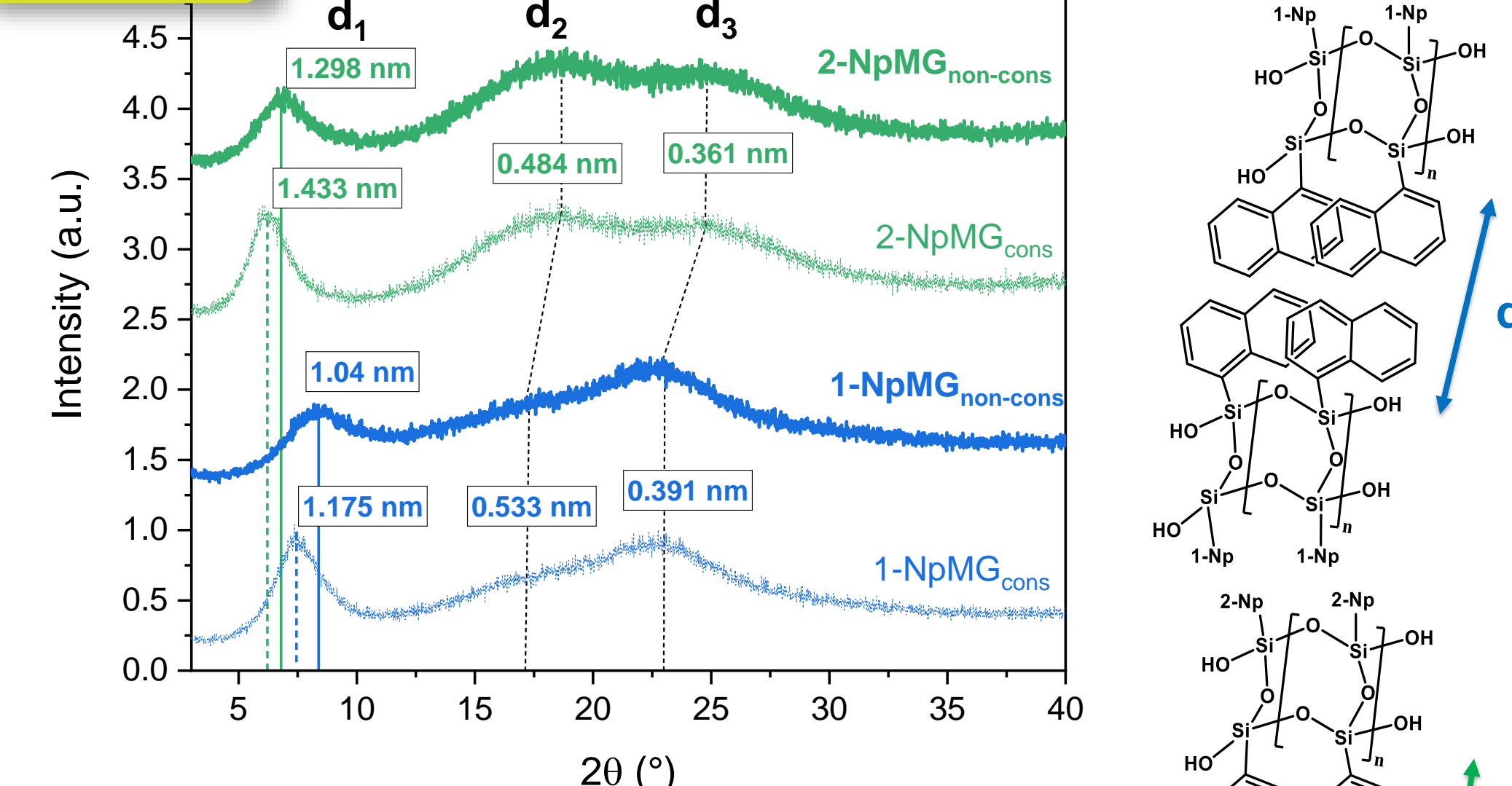
- low molecular weight in the non-consolidated state → only oligomeric units
- 1-NpMG after consolidation still low molecular weight
- M(1-NpMG) < M(2-NpMG)

## Characterization



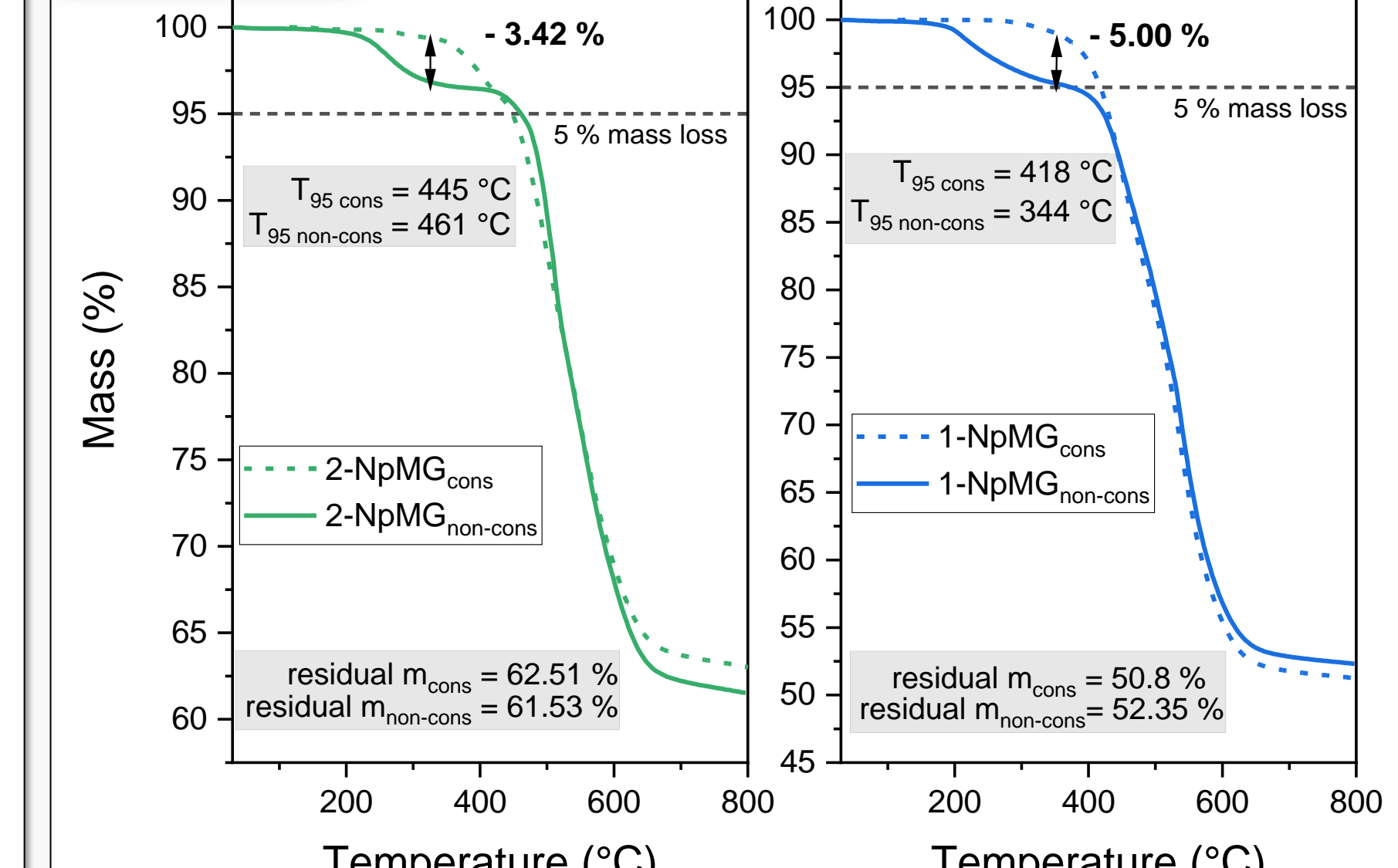
- still OCH<sub>3</sub>- and OH-groups in the non-consolidated and consolidated gel.
- after consolidation, only small amount of isolated OH-groups → no further condensation reactions possible

## PXRD



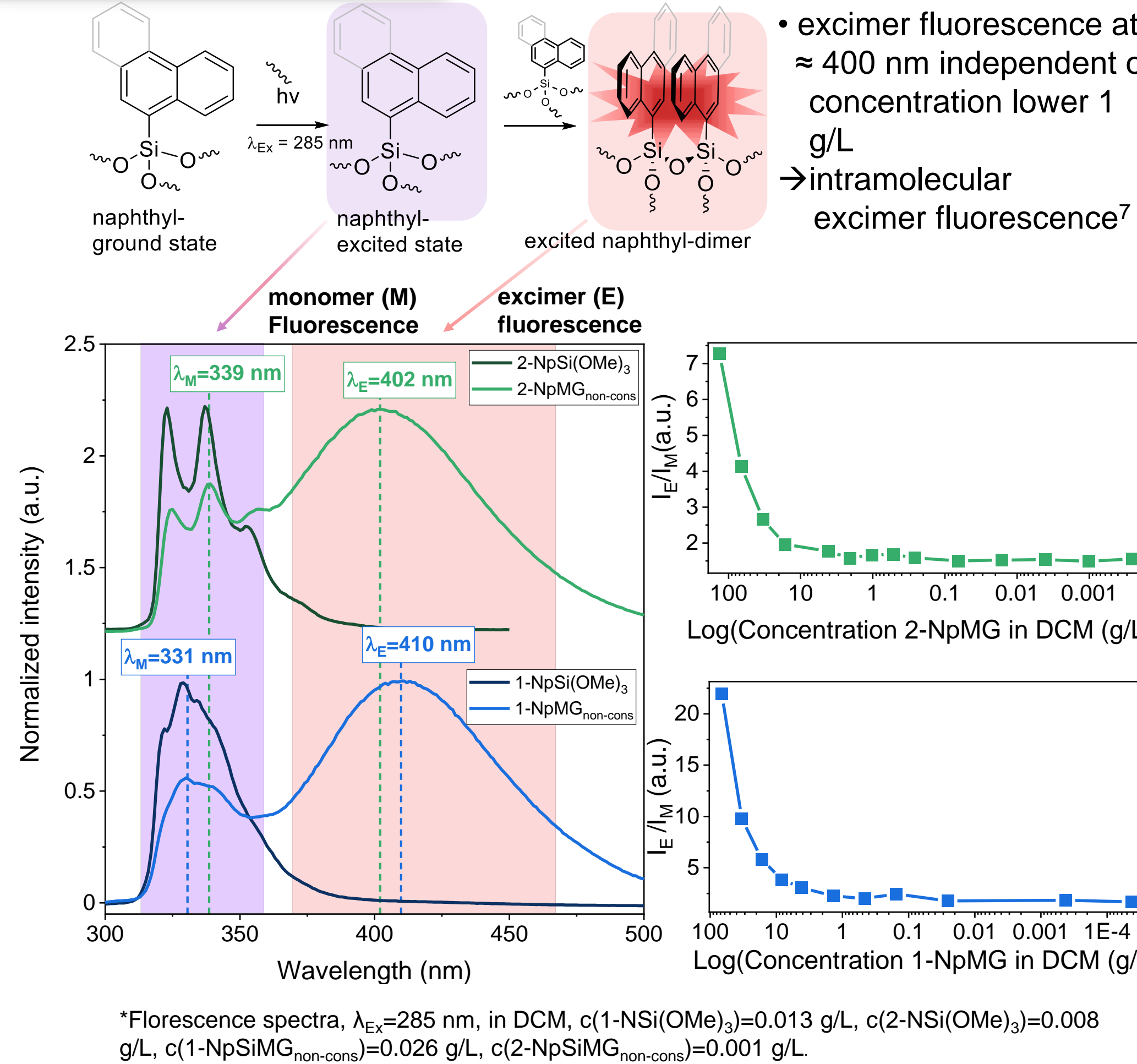
- amorphous peaks → reported for ladder structures<sup>4</sup> (d<sub>1</sub> = intermolecular chain-to-chain distance, d<sub>2</sub> = average thickness of ladder) and POSS-systems<sup>5</sup> (d<sub>1</sub> = distance between cubes, d<sub>2</sub> = diagonal and d<sub>3</sub> = distance between the Si<sub>4</sub>O<sub>4</sub> faces)
- ladder-like or cage domains, but defect-rich structure
- d<sub>1</sub>(2-Np) > d<sub>1</sub>(1Np) → higher expansion of organic group<sup>6</sup>
- consolidation results in a shift of d<sub>1</sub> and an increasing intensity → further condensation reactions → reorientation of structure, higher number of ordered domains, but still defect rich.

## TGA



- 1<sup>st</sup> mass loss by further condensation reactions → loss of by-products H<sub>2</sub>O and MeOH
- 1-NpMG lower condensation degree → more condensation reactions possible → larger 1<sup>st</sup> mass loss → lower residual mass
- high thermal stability > 400 °C

## Fluorescence



- excimer fluorescence at ≈ 400 nm independent of concentration lower 1 g/L → intramolecular excimer fluorescence<sup>7</sup>

## Conclusion

Our investigations show that the organic group has a significant influence on the melting gel properties. Trialkoxysilanes with naphthyl substituents can be hydrolysed and condensed under standard conditions, forming melting gel-like, transparent, and reversibly softenable materials. However, there is a difference in the reactivity of the isomers. The 2-naphthyl group shows facilitated hydrolysis and condensation compared to the 1-naphthyl group, resulting in enhanced crosslinking. The high crosslinking and the increased number of hydrolysed groups lead to an irreversibly curing by further thermal treatment. It is expected that the sterically demanding residue of the 1-NpSi(OMe)<sub>3</sub> lowers the hydrolysis and condensation rate and preferentially leads to intramolecular condensation reactions<sup>5</sup>, caused in a lower network formation and no irreversible curing. In general, both materials exhibit ladder-like structural motifs and possibly cage-like structures. Furthermore, intramolecular interactions of the aromatic groups could be detected, as well as interacting OH groups that thermally condense at 200 °C. These studies provide important insight into the role of substituents in the synthesis and properties of novel melting gels.

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