

Perylene Polyphenylmethylsiloxanes for Optoelectronic Applications

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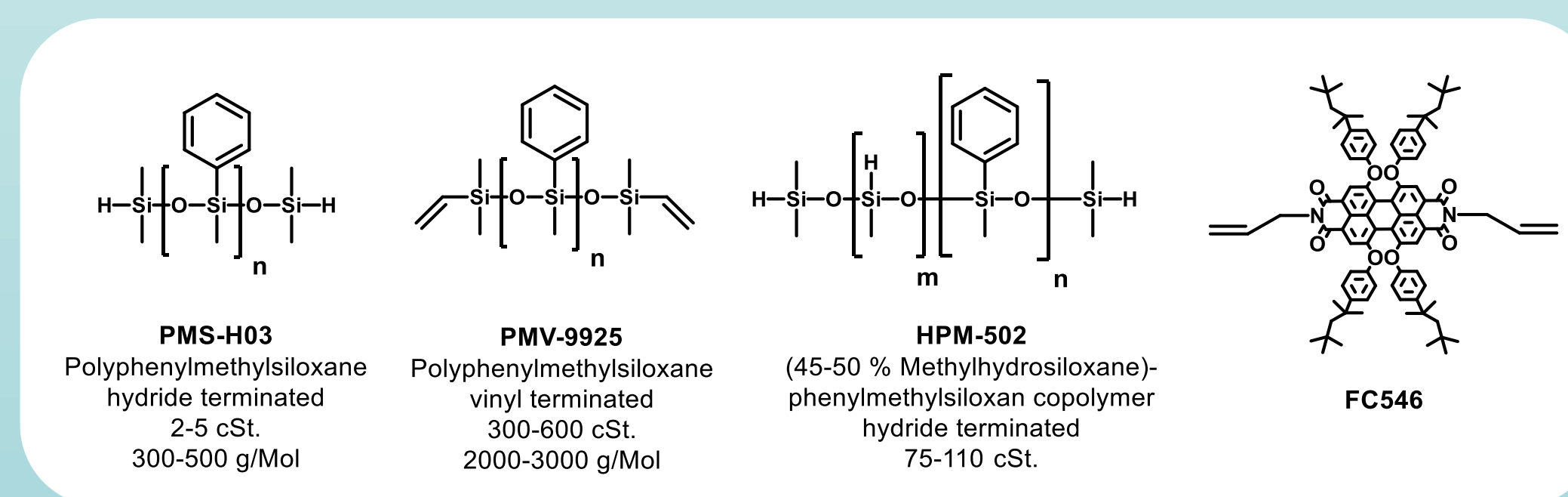
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Introduction

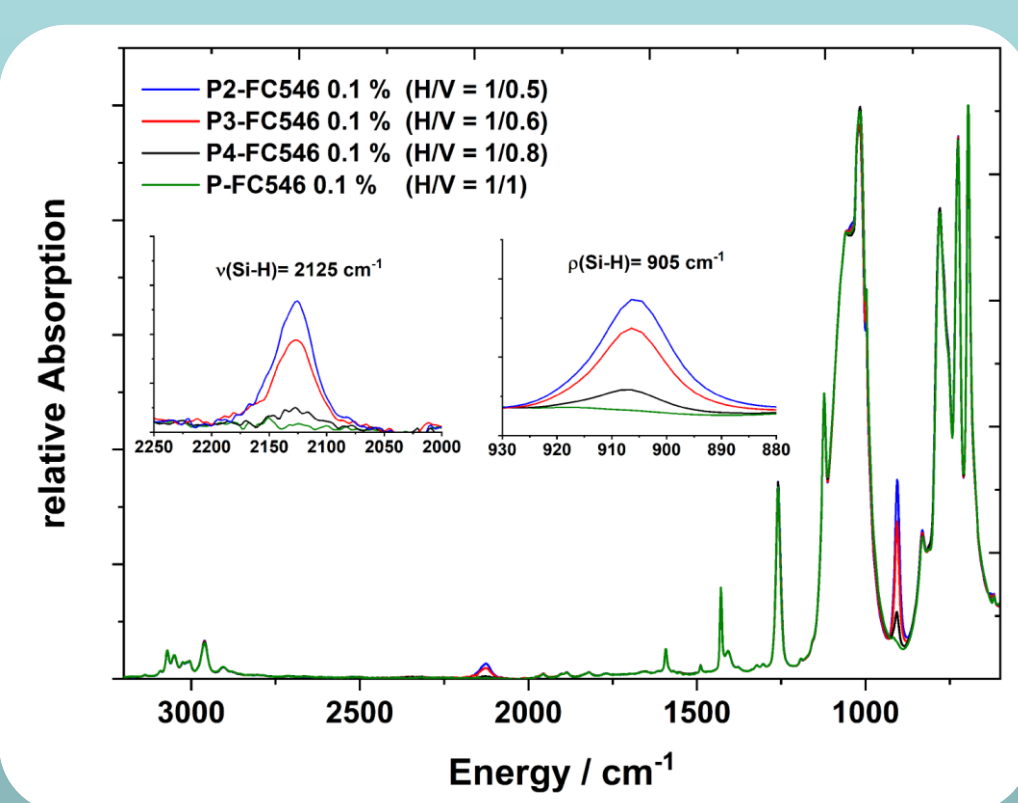
Organic alternatives for inorganic rare earth containing conversion materials in Light Emitting Diodes (LED) are an object of present research.^[1-4] Organic dye based converters are also attractive for clean and renewable energy generating applications, such as new efficient materials for photovoltaics and luminescent solar collectors (LSC). Quite stable and promising candidates for both types of applications are perylene diimide derivatives.^[5-9] Due to the limited solubility of perylene dyes in polysiloxanes new methods have to be found to increase the dye concentration for higher device efficiencies.^[1,10] In the presented study, the allyl group containing perylene diimide dye FC546 was used to synthesize two different perylene polysiloxanes with various dye concentrations (0.025 and 8 wt%) in the backbone of a polymethylphenylsiloxane (PMPS) and cross-linked to the pendant hydride groups of a methylhydrosiloxane-phenylmethylsiloxan copolymer.^[11] Both polymer classes were synthesized by a platinum catalyzed hydrosilylation reaction. By changing the ratio of the hydride and vinyl terminated PMPS precursors the chain length was modified systematically (5660 - 8400 g mol⁻¹). Subsequently the liquid perylene polymers were covalently integrated in a thermally curable phenyl containing HRI polysiloxane resin, showing high thermal stabilities (>430 °C), high quantum yields (>97 %) and tunable hardness. While linear and cross-linked polymers with perylene derivatives incorporated have already been published, the resulting materials are not suitable for a subsequent covalent integration into a curable matrix system by hydrosilylation.^[12-15]

Synthesis of highly fluorescent Perylene Polyphenylmethylsiloxanes

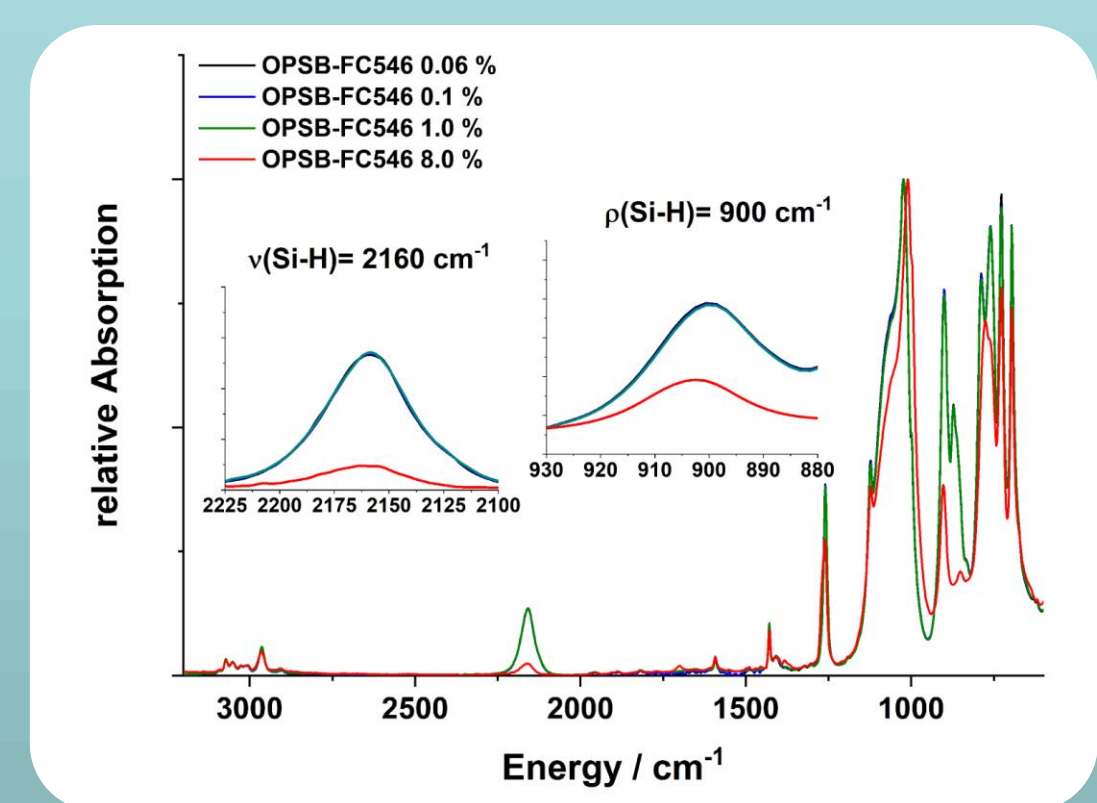
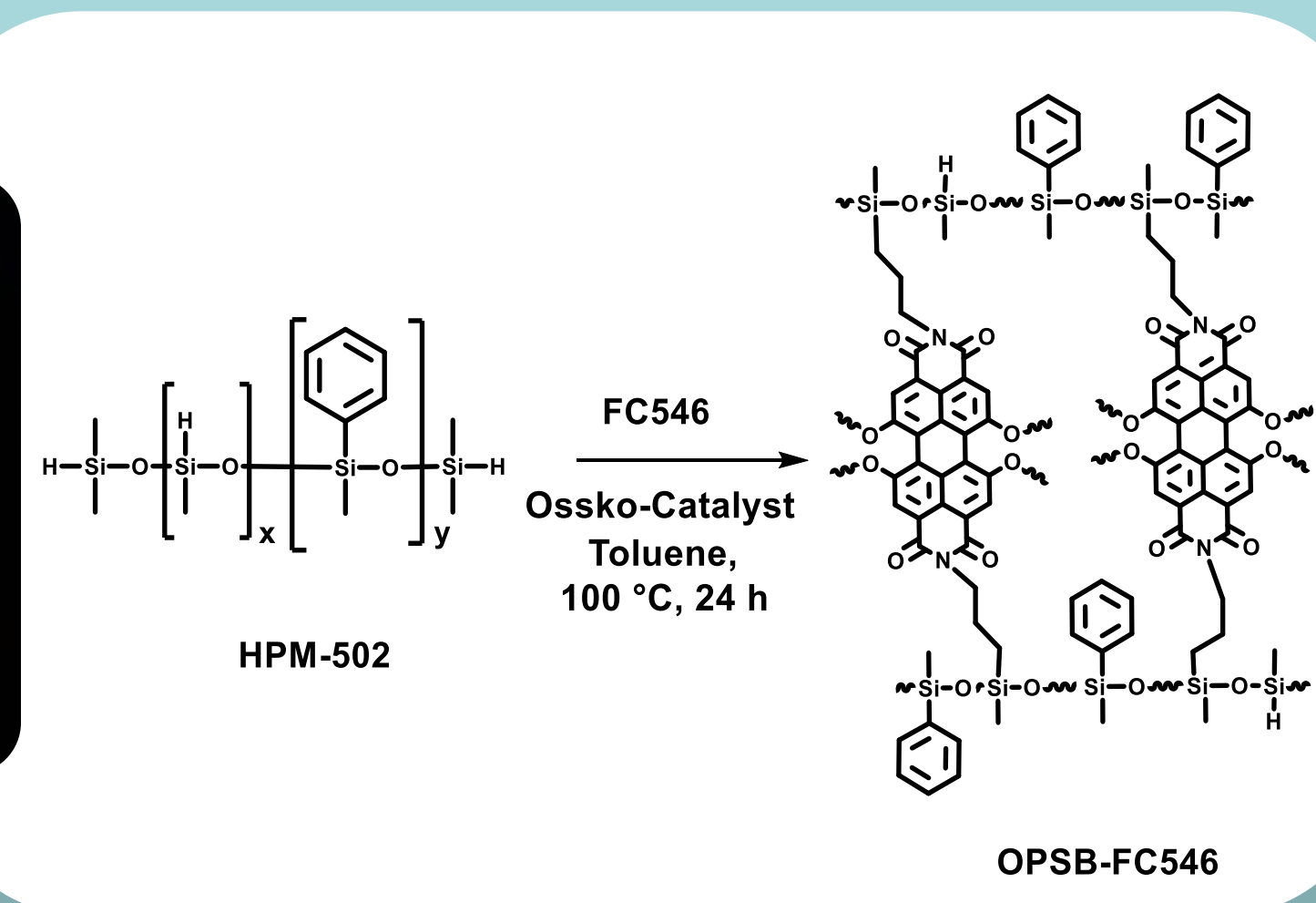
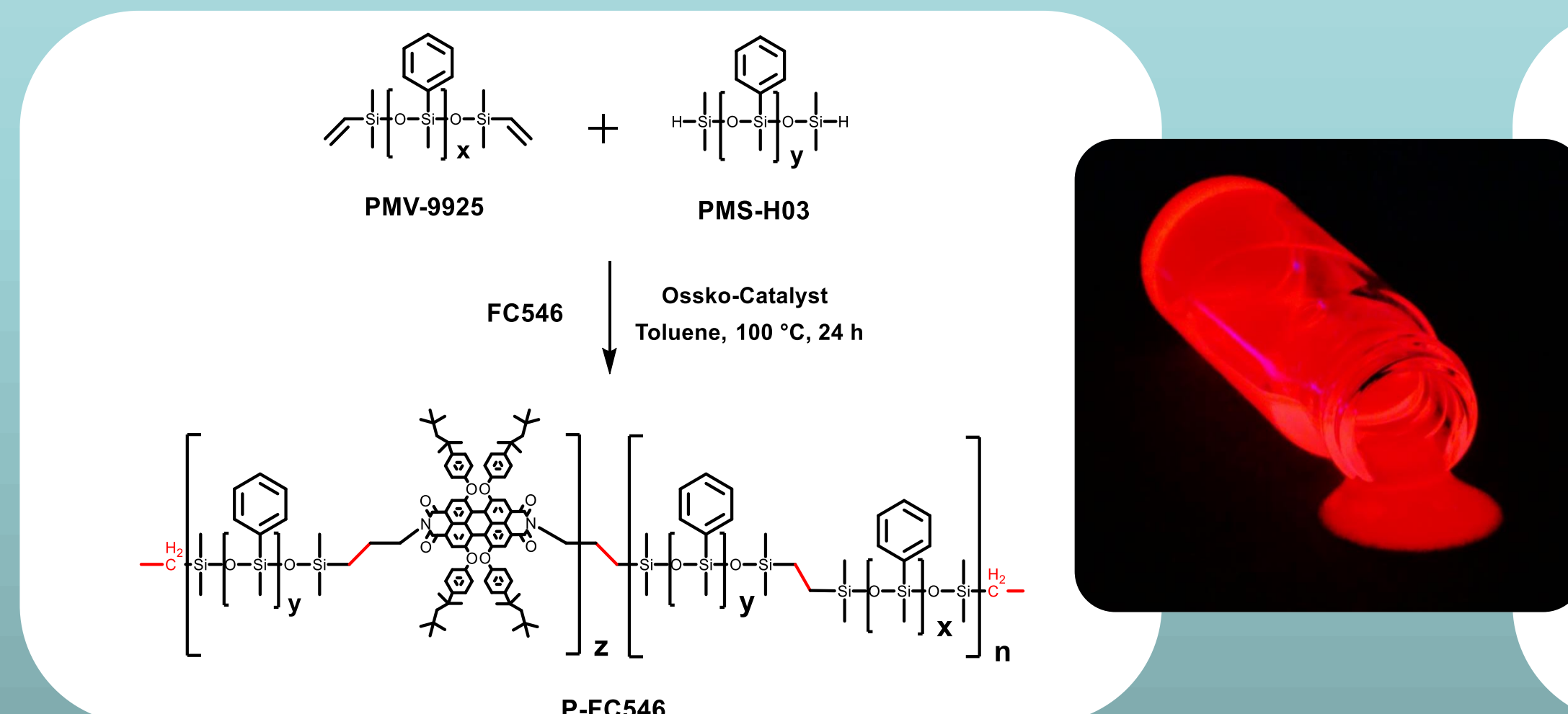
Perylene linearly attached to the polymer backbone



Perylene cross-linked between chains

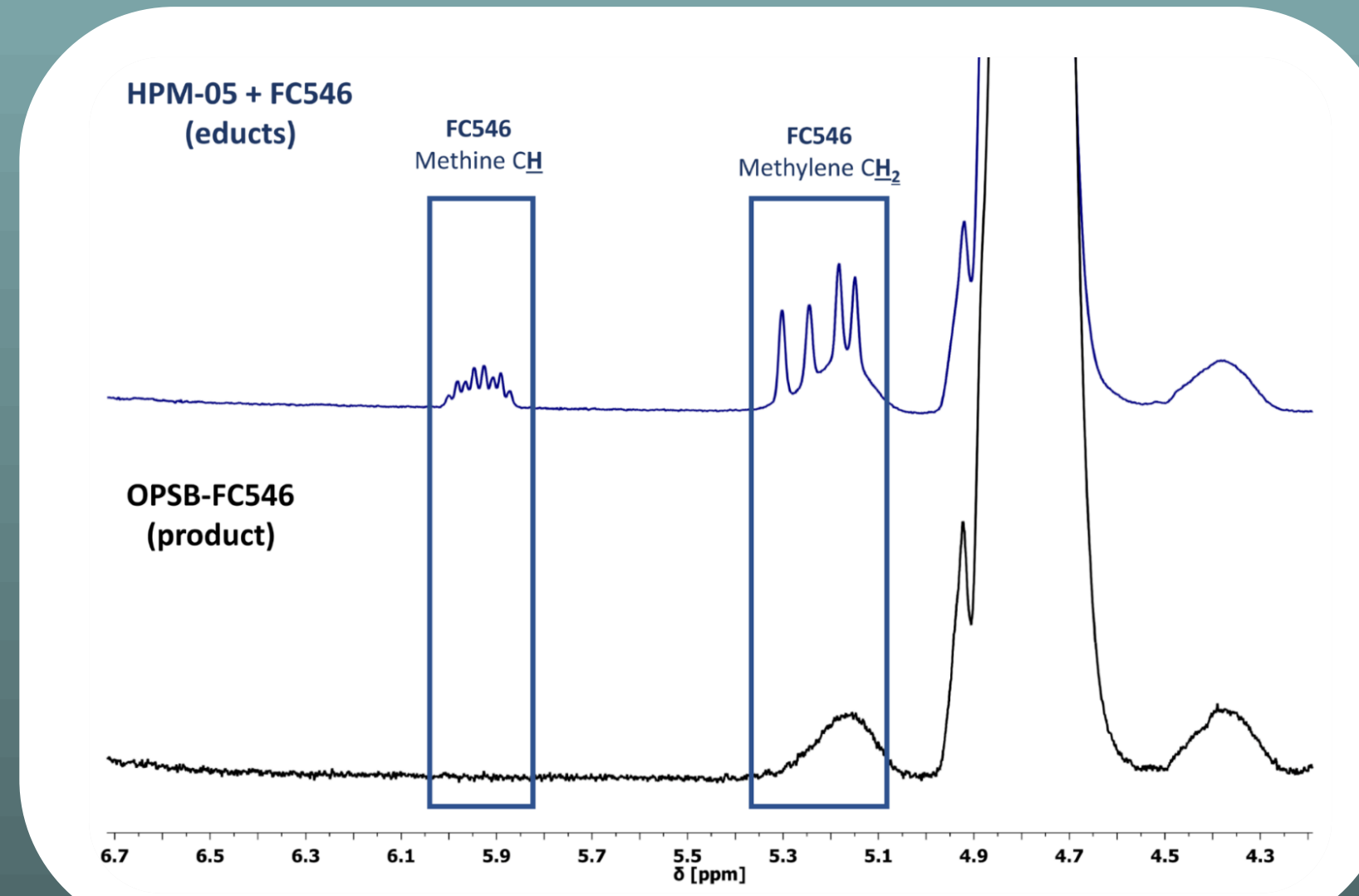


FTIR spectra of P-FC546 and the PX-FC546 - 0.1 % series with x=2, 3, 4.



FTIR spectra of the OPSB-FC546 - X % series with X=0.06, 0.1, 1.0 and 8.0.

Sample	M _w / g mol ⁻¹	D
PMS-03	420/400*	1.1
PMV-9925	2500/2500*	2.4
P4-FC546 0.1 %	8400	1.9
P3-FC546 0.1 %	6080	1.7
P2-FC546 0.1 %	5660	1.7



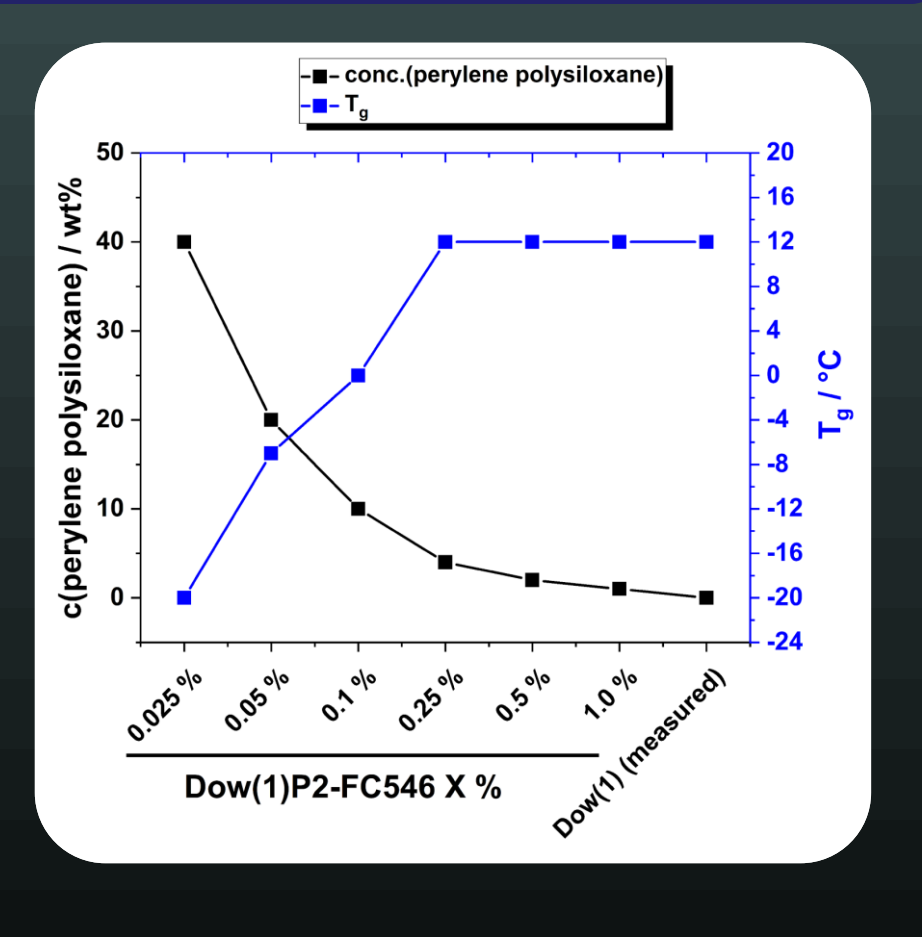
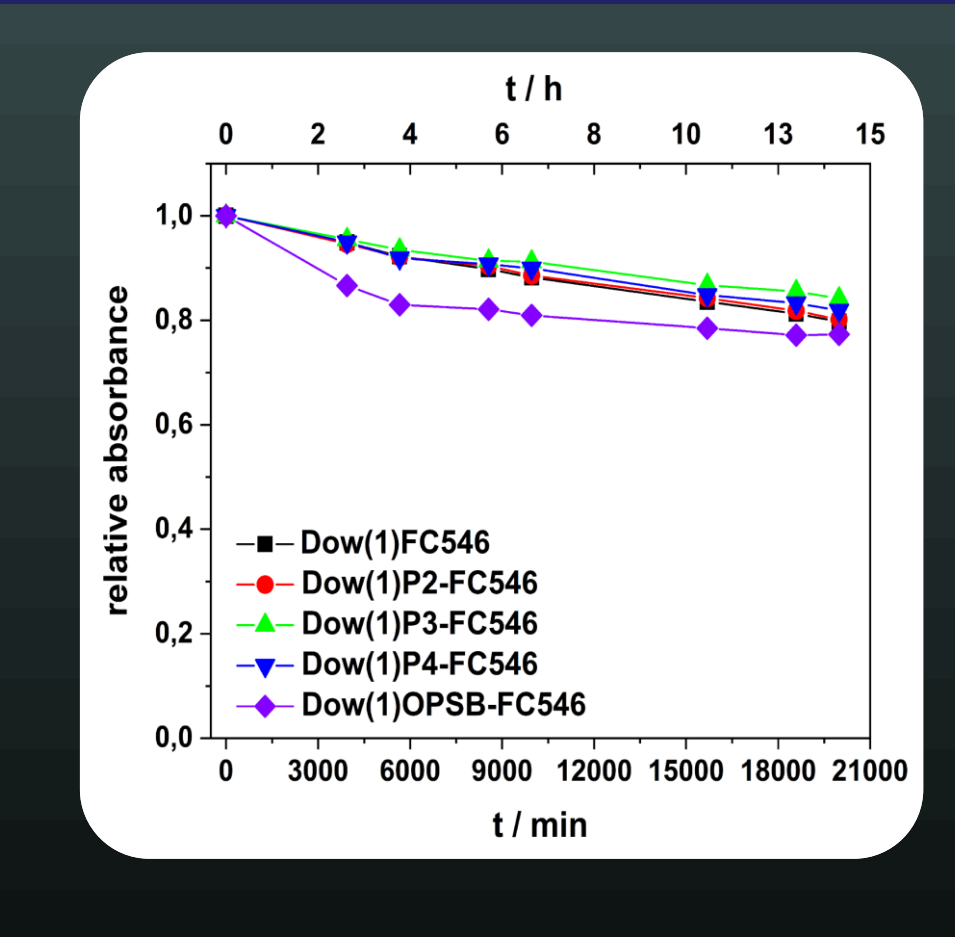
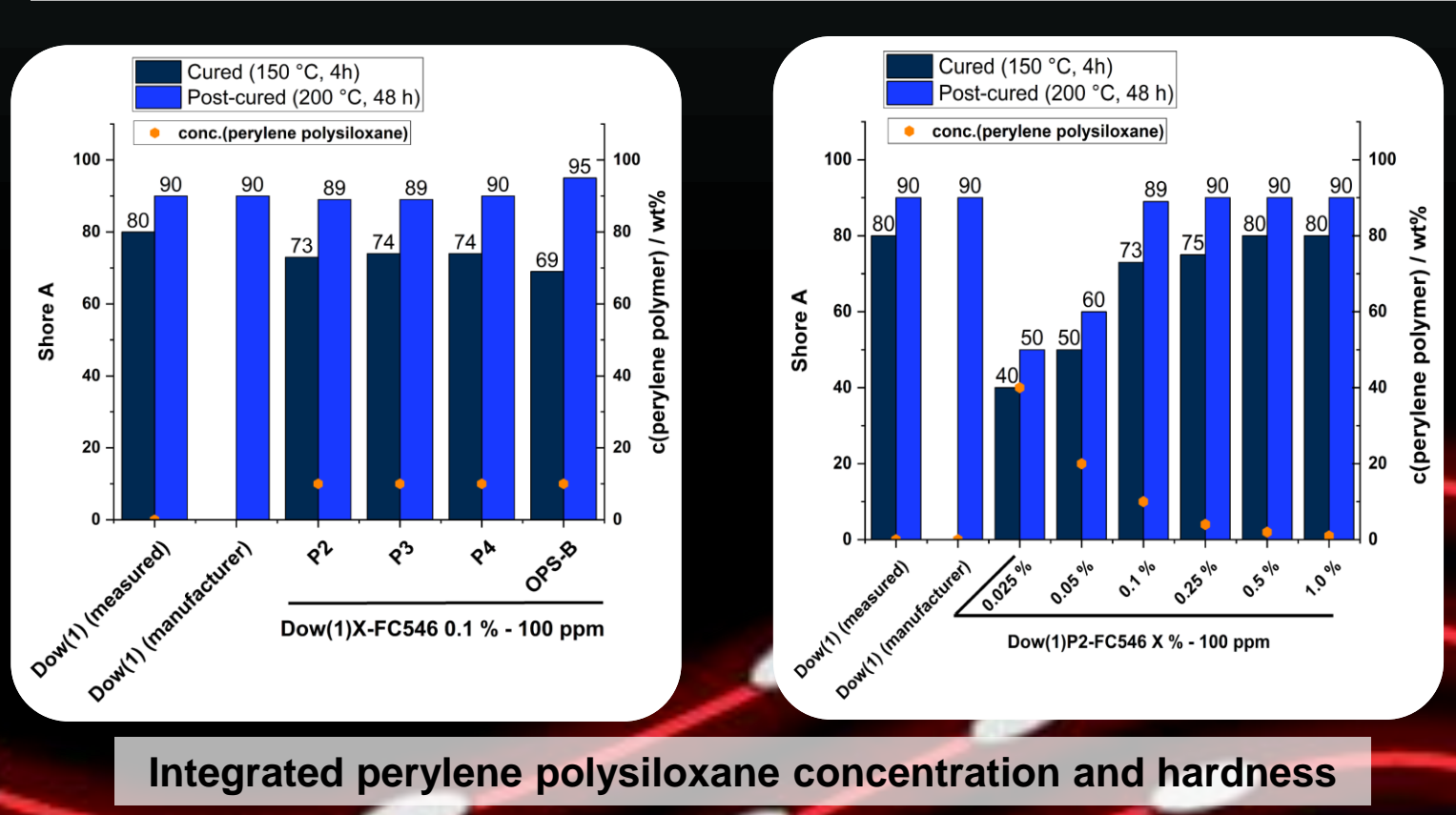
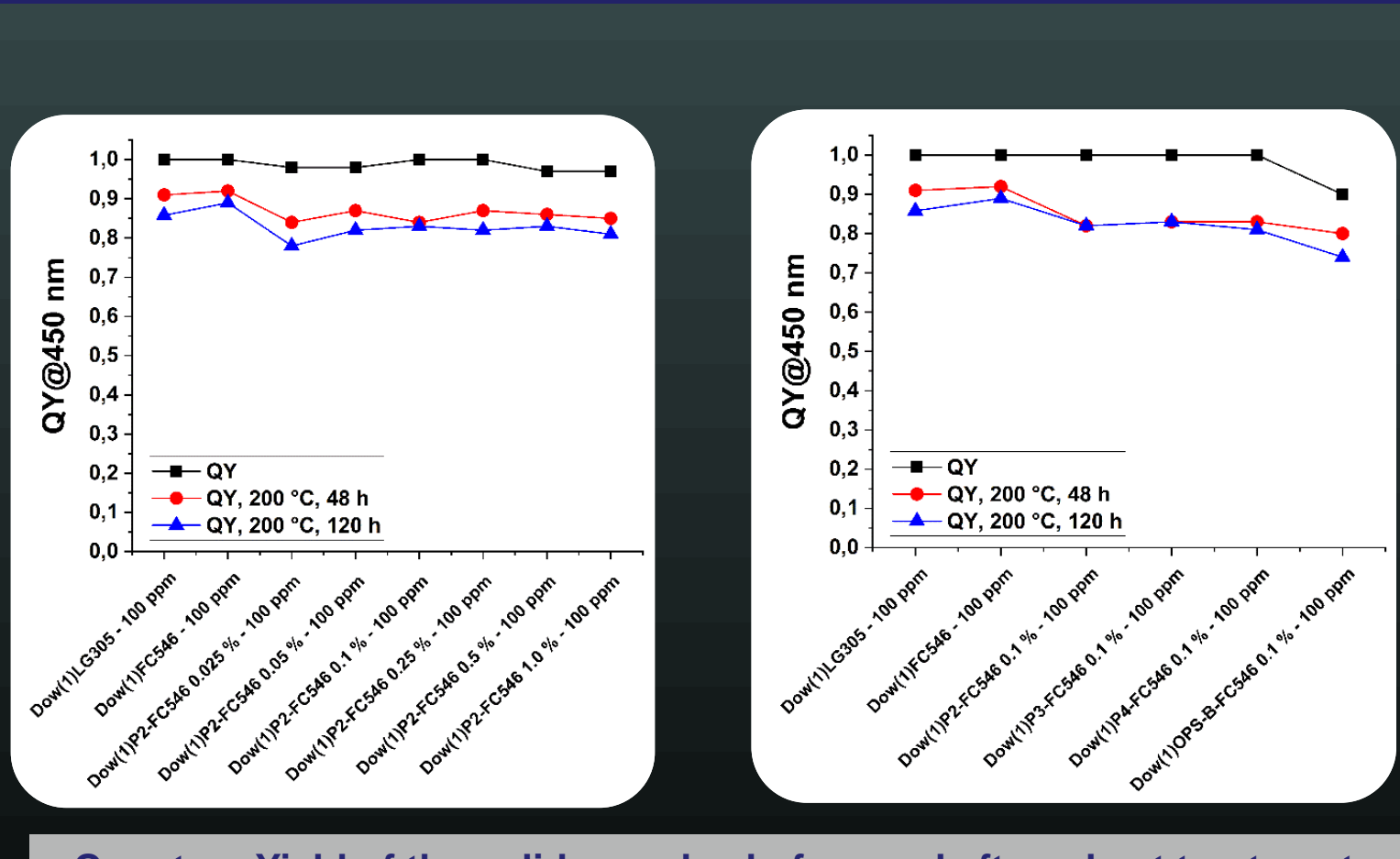
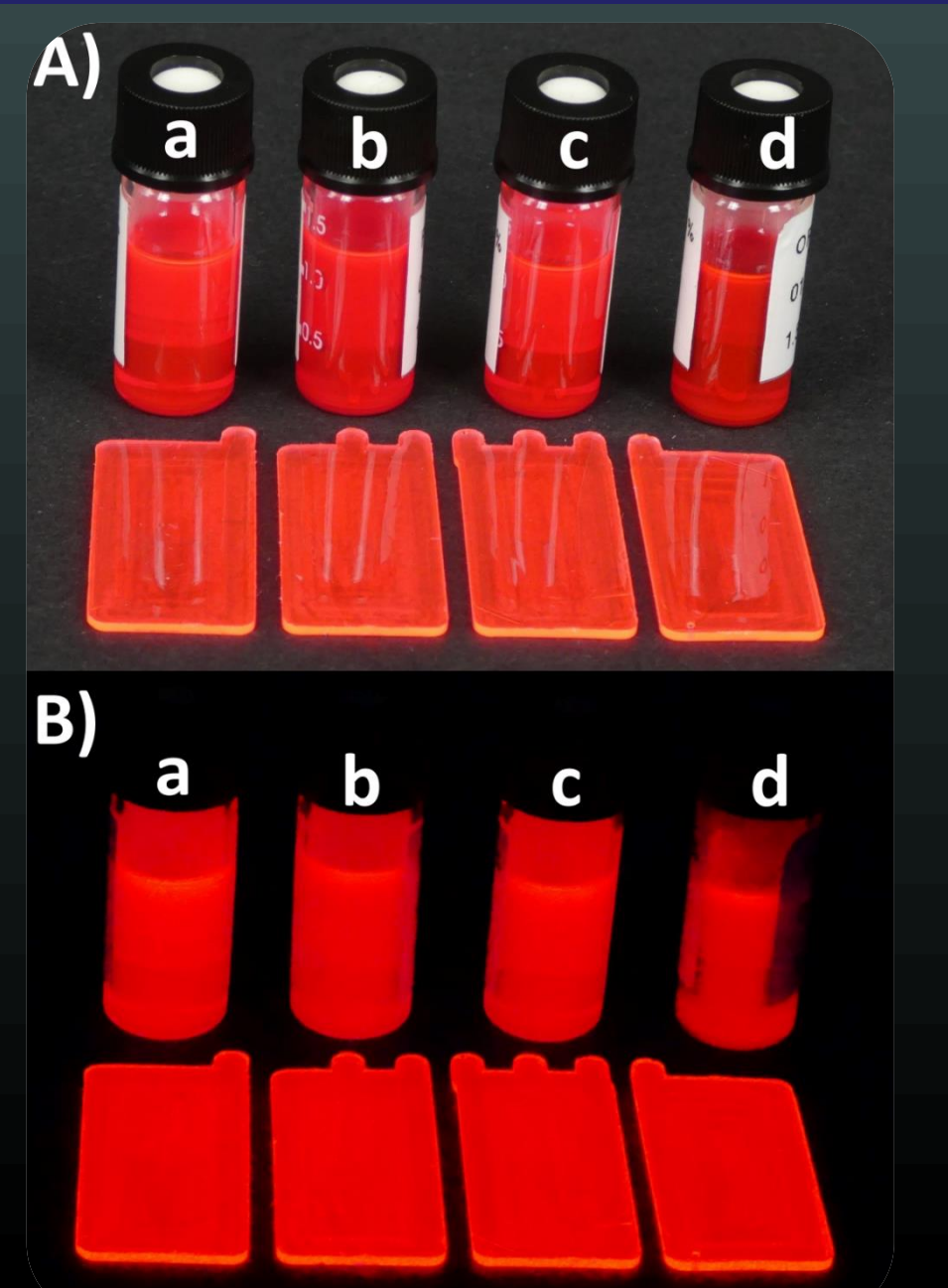
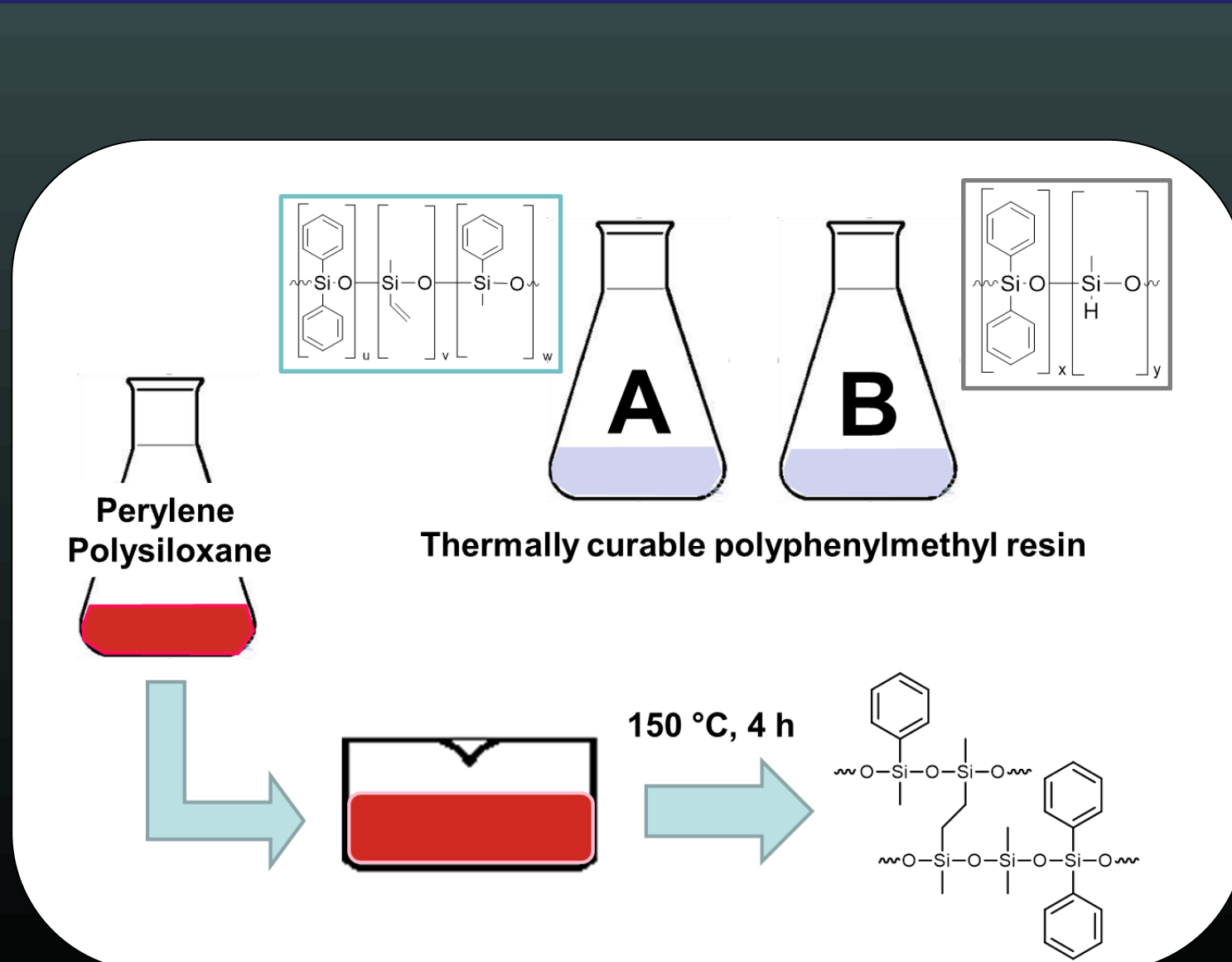
¹H NMR spectra of OPS-B-FC546 8% before and after the hydrosilylation reaction measured in chloroform-D. The covalent integration is verified by the decrease of methine and methylene proton signals from the allyl groups if FC546.

Sample	m(FC546) / mg	n(FC546) / μmol	c(FC546) / %
OPSB-FC546 - 0.1 %	0.5	0.38	0.10
OPSB-FC546 - 1.0 %	5.0	3.88	1.00
OPSB-FC546 - 8.0 %	40.0	31.06	8.00

- Successful integration of perylene to polymer backbone
 - Highly fluorescent and liquid polymers obtained
- Increased hydride/vinyl ratio leads to increased molecular weight
- Increased ratio can be verified by FTIR and NMR spectroscopy
 - High concentration of dye incorporable (up to 8 wt%)
 - High quantum yields >80 %
- Chains can be covalently integrated to other resin by hydrosilylation

- Integration of perylene cross-linked between polymer chains
 - Highly fluorescent and liquid polymers obtained
- Covalent integration can be verified by FTIR and NMR spectroscopy
 - High concentration of dye incorporable (up to 8 wt%)
 - High quantum yields >80 %
- Chains can be covalently integrated to other resin by hydrosilylation

Curable Encapsulation Integration and Characterization



- Samples with high QY even after 120 h @ 200 °C (>80 %)
- High thermal stability (>430 °C)
- Hardness of the samples decreases with increasing amount of integrated linear perylene polysiloxanes
 - Decreasing T_g verifies lowered cross-linking degree
 - Tunable hardness for different applications (50 - 90 SA)
- ✓ High dye concentrations and excellent properties making this Materials suitable for many applications like LED or LSC

References, funding and cooperation

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