Supplementary Information

The supplementary information contain:

- The deconvolution of spectra in individual components
- Equations used for the quantifications

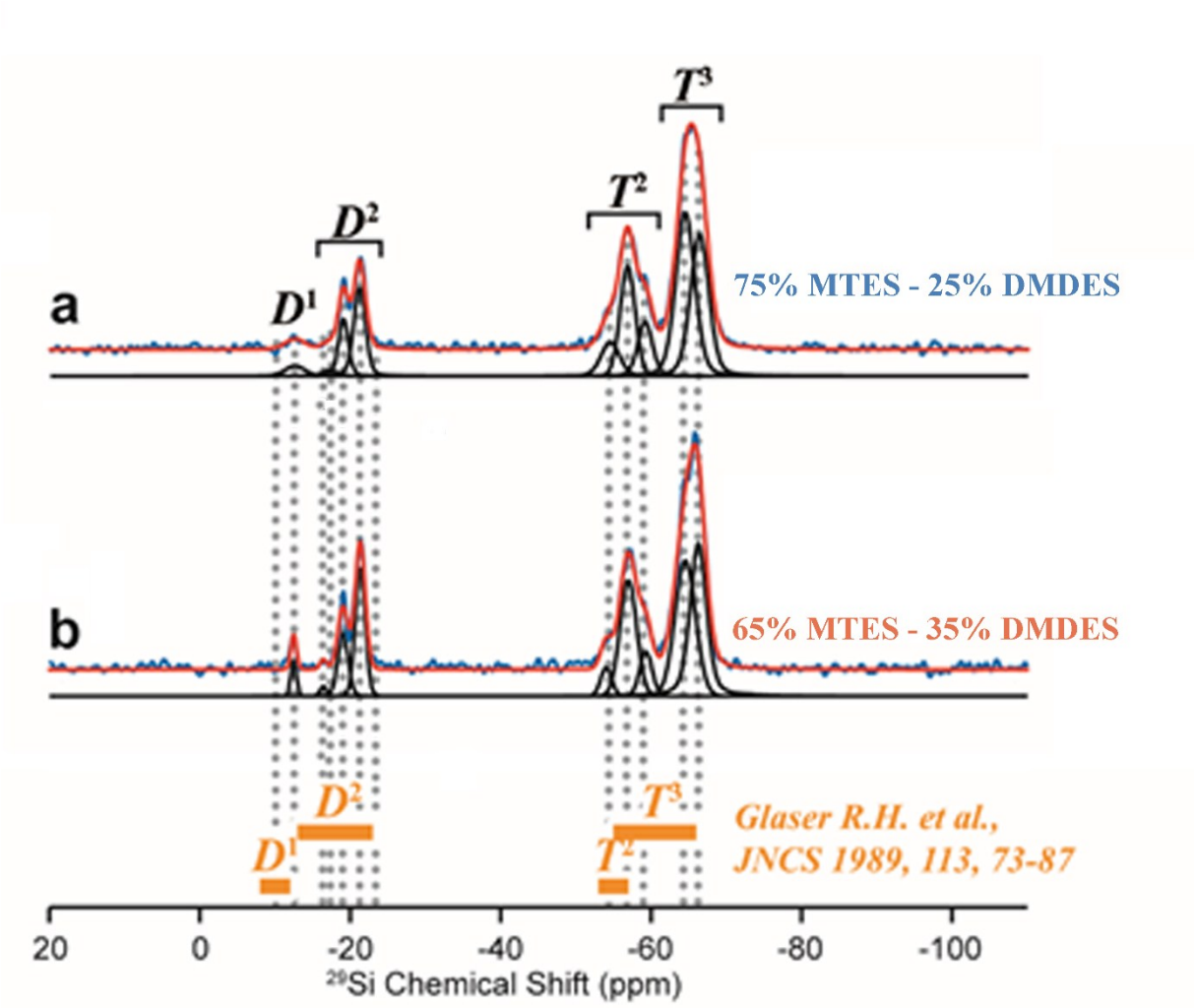

Figure S1. Quantitative ^{29}Si echo-MAS NMR spectra (in blue) collected for the studied hybrid glasses. In red are models obtained for each sample from a simultaneous fit of multiple spectra (including ^{29}Si echo-MAS with different recycling delays and ^{29}Si[^{1}H] CP-MAS spectra with different contact times, not shown) with a single set of parameters (number of peaks, positions, width and Gaussian/Lorentzian ratio). The individual components used for the fits are shown in black below.

Equations used for the quantifications.

Fixing an arbitrary number of C atoms $n_{C,tot}$ (e.g. $n_{C,tot} = 100$), one can then derive the number of carbons attributed to Me_2Si and MeSi groups that can be expected based on the ratios of MTES and DMDES precursors used for the synthesis (n_{MTES}/n_{DMDES}). These numbers need to take into account the relative integrated intensities of carbon signals in **C**H_2-O and **C**H_3-CH_2-O environments: I_{C,CH_2-O} and I_{C,CH_3-CH_2-O}.

$$n_{C,Me_2Si} = I_{C,Me_2Si} n_{C,tot} = n_{C,tot} \frac{1 - I_{C,CH_2-O} - I_{C,CH_3-CH_2-O}}{1 + 0.5(n_{MTES}/n_{DMDES})}$$

where the 0.5 comes from there being 2 C atoms per DMDES molecule. Similarly:

$$n_{C,MeSi} = I_{C,MeSi} n_{C,tot} = n_{C,tot} \frac{1 - I_{C,CH_2-O} - I_{C,CH_3-CH_2-O}}{1 + 2(n_{DMDES}/n_{MTES})}$$

These numbers impose in turn the number of Si atoms $n_{Si,tot}$:, which relates to the relative integrated intensities of Si T^n and D^n species:

$$n_{Si,tot} = n_{Si,tot} \sum_{i = 0...3} I_{Si,T^i} + n_{Si,tot} \sum_{i = 0...2} I_{Si,D^i} = n_{C,MeSi} + 0.5 n_{C,Me_2Si}$$

From there we can compare the number of unreacted Si-O-Et groups, given by:

$$n_{O-CH_2-CH_3} = n_{C,tot} I_{C,CH_3-CH_2-O} = n_{C,tot} I_{C,CH_2-O}$$

with the number of incompletely-condensed Si sites, *i.e.* D^n with n < 2 and T^n with n < 3. (This comparison is simple here because we observe only D^1 and T^2 sites, meaning that there is no more than one uncondensed O atom per Si):

$$\sum_{i = 0...1} n_{Si,D^i} + \sum_{i = 0...2} n_{Si,T^i} = \left(n_{C,MeSi} + 0.5 n_{C,Me_2Si}\right)\left(\sum_{i = 0...3} I_{Si,T^i} + n_{Si,tot} \sum_{i = 0...2} I_{Si,D^i} \right)$$

The difference between these numbers should correspond to the number of silanol groups.