

Supplementary Information for

The Existence of a Strongly Bonded Layer in Associating Liquids within Silica Pores - the Spectral and Molecular Dynamics Study

Natalia Soszka^a, Magdalena Tarnacka^{b*}, Barbara Hachuła^a, Patryk Włodarczyk^c,
Roman Wrzalik^b, Marian Paluch^b, Marek Hreczka^{c,d}, Kamil Kamiński^b

^a Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, 40-006 Katowice, Poland

^b August Chelkowski Institute of Physics, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

^c Lukasiewicz Research Network – Institute of Non-Ferrous Metals, ul. Sowinskiego 5, 44-100 Gliwice, Poland

^d Department of Mechatronics, Silesian University of Technology, Akademicka 10A St., 44-100, Gliwice, Poland

*Corresponding author: magdalena.tarnacka@us.edu.pl

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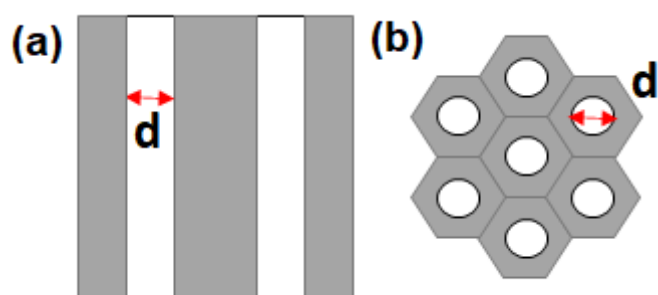


Fig. S1. The schematic structure of cross-section (a) and the top (b) of applied silica mesopore templates.

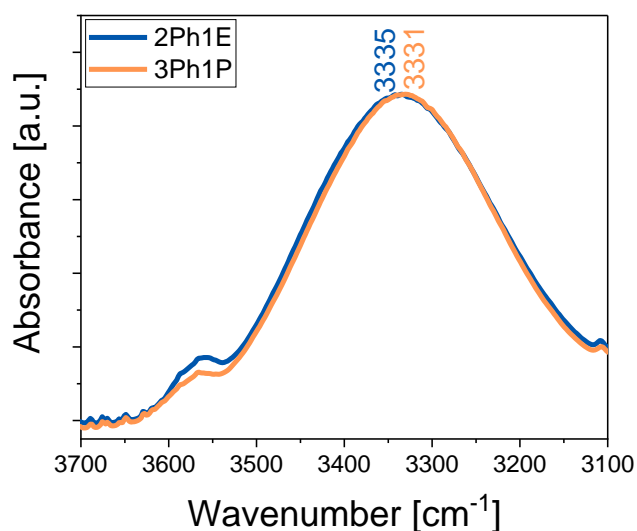


Fig. S2. The normalized infrared spectra of bulk MAs in the frequency region 3700 – 3100 cm^{-1} showing the stretching vibration of the OH groups.

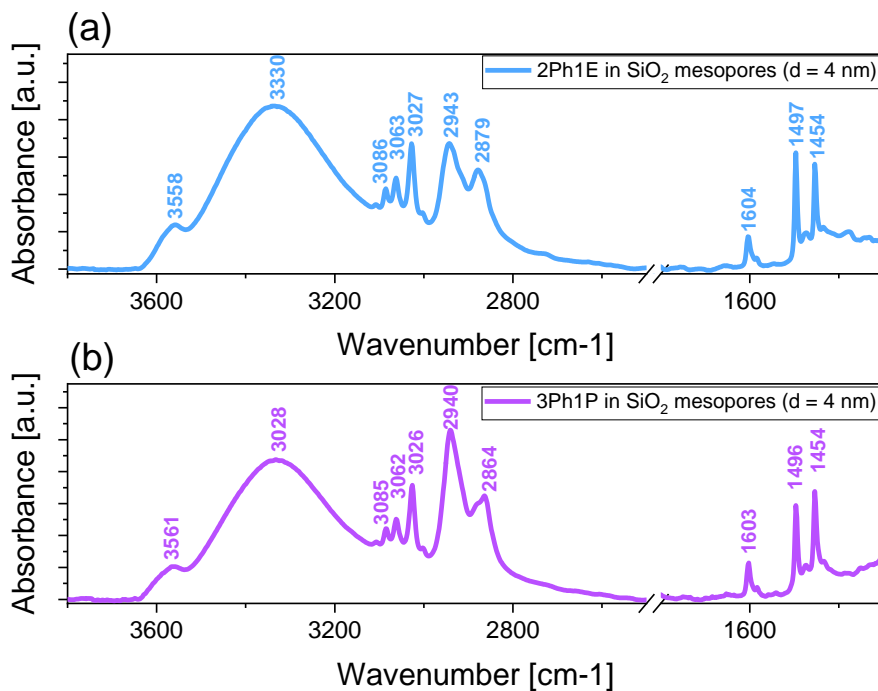


Fig. S3. IR spectra of (a) 2Ph1E and (b) 3Ph1P infiltrated into native silica mesopores ($d = 4$ nm) at 297 K in the spectral regions $3800 - 2500$ cm^{-1} and $1800 - 1300$ cm^{-1} .

The vibrational analysis of 2Ph1E and 3Ph1P was performed based on the reported theoretical spectra in the literature. **Fig. S3** shows IR spectra of 2Ph1E and 3Ph1P infiltrated into silica nanopores measured at 293 K in the frequency range $3800\text{-}1300$ cm^{-1} , respectively. The spectra are shown only to 1300 cm^{-1} because, in the lower wavenumber region, there was an oversaturation caused by the silica matrix. In the upper-frequency region, one can observe the bands corresponding to the stretching vibration of hydroxyl groups ($3650 - 3100$ cm^{-1}). The absorption signals in the region $3100 - 3000$ cm^{-1} are assigned to the aromatic C-H stretching vibrations, and the peaks related to the asymmetric and symmetric aliphatic C-H stretching vibrations lie between $3000 - 2800$ cm^{-1} . A sharp band originating at 1604 cm^{-1} (2Ph1P) and 1603 cm^{-1} is due to ring deformation vibration. Additionally, for 2Ph1P, the visible peak located at 1497 cm^{-1} is related to the mixed C-H ring bending and ring deformation vibrations. For 3Ph1P, the band observed at 1496 cm^{-1} is characterized by the CH₂ scissoring vibration. A peak of small intensity at 1474 cm^{-1} corresponds to the CH₂ scissoring vibrations (2Ph1P). Absorption signals occurring at 1454 cm^{-1} in both alcohols are due to the mixed aromatic C-H ring bending vibrations, ring deformations, and CH₂ scissoring vibrations for 2Ph1P, and the CH₂ wagging vibration mixed with the OH in-plane deformation for 3Ph1P.

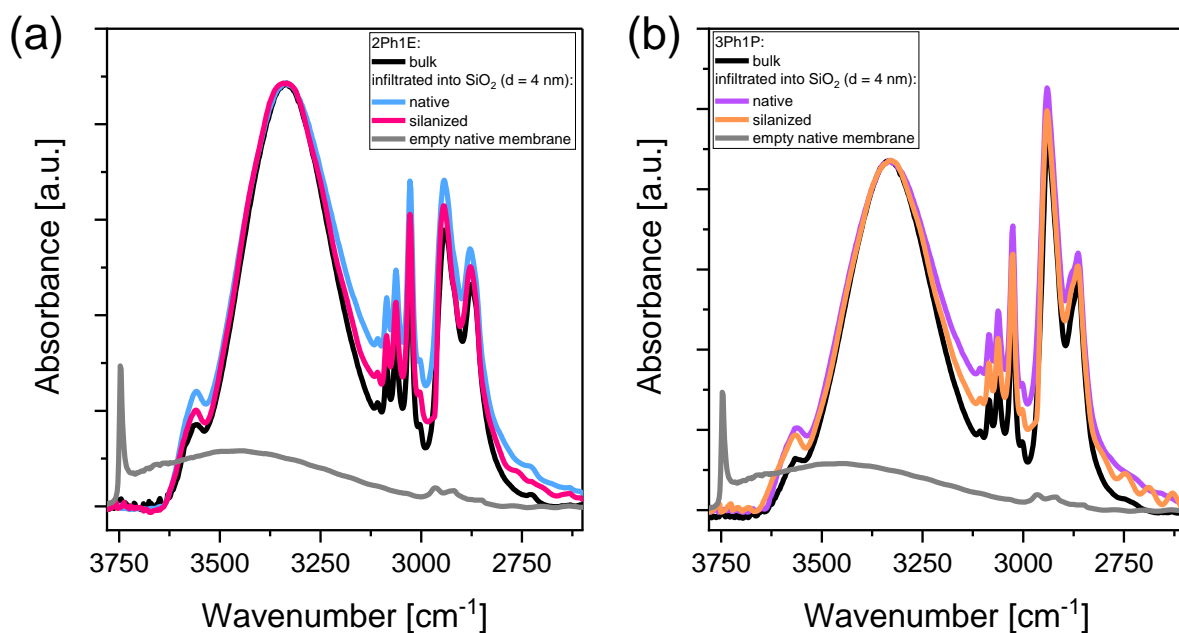


Fig. S4. Infrared spectra of the bulk 2Ph1E (a) and 3Ph1P (b) together with those obtained for PhAs infiltrated into native and silanized silica templates of $d = 4$ nm measured at $T = 297$ K in the spectral region $3800 - 2600$ cm^{-1} . The spectra were normalized to the OH stretching vibration peak. Additionally, a spectrum of empty silanized silica templates was added.

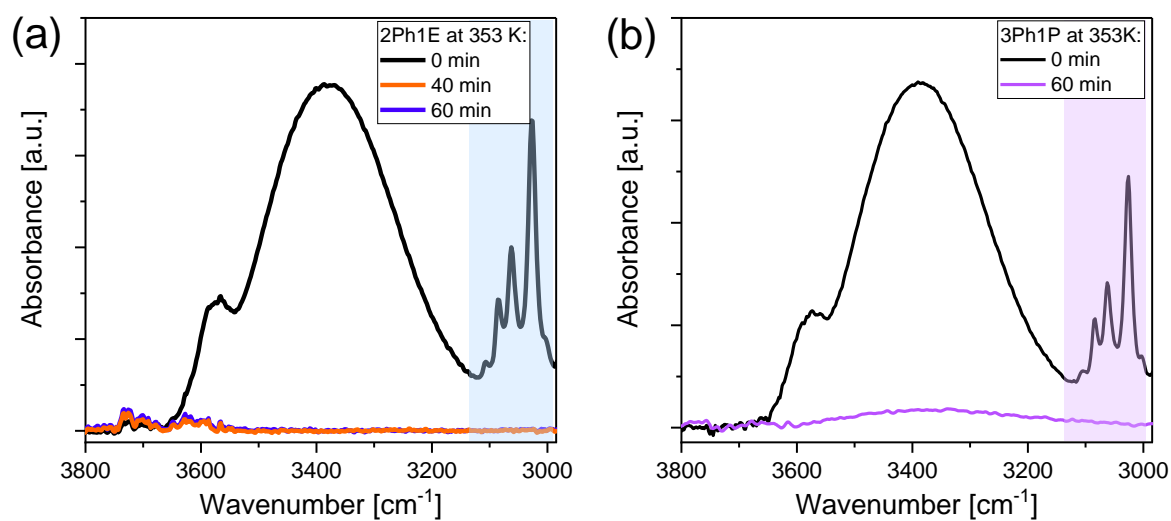


Fig. S5. FTIR spectra of bulk 2Ph1E (a) and bulk 3Ph1P (b) at $t = 0$ min and $t = 60$ min in the frequency region $3800 - 3000$ cm^{-1} .

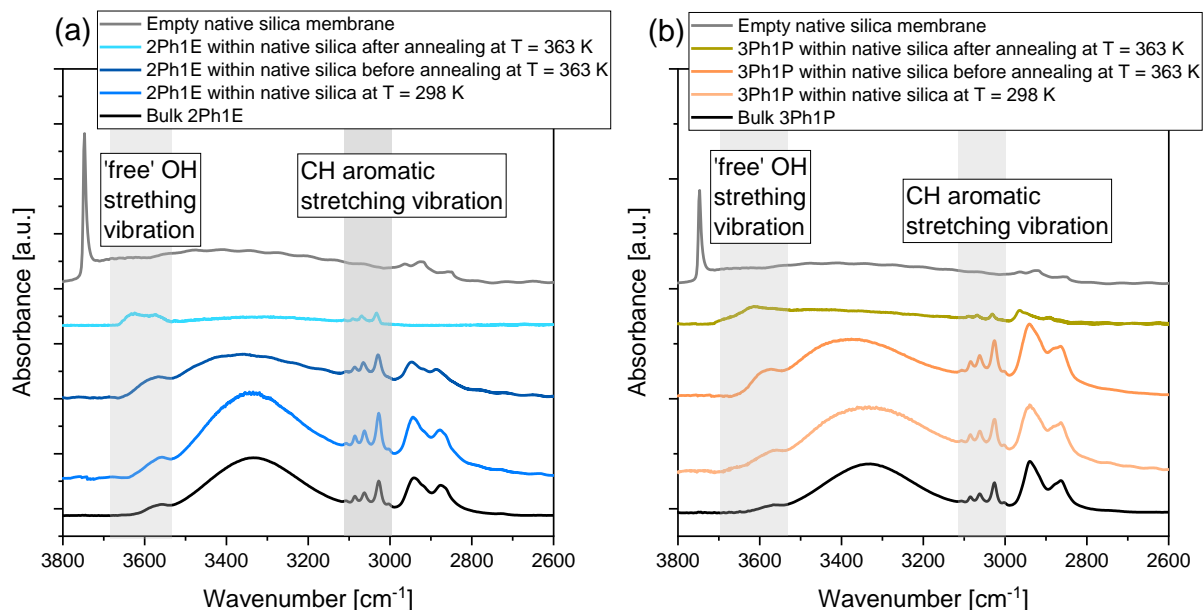


Fig. S6. The comparison of FTIR spectra recorded in the spectral region $3800 - 2600 \text{ cm}^{-1}$ for (a) 2Ph1E and (b) 3Ph1P of the bulk and infiltrated into native silica mesopores of $d = 8 \text{ nm}$ at 298 K and also before and after the evaporation. For comparison, the FTIR spectrum of “empty” native silica membrane was also added.

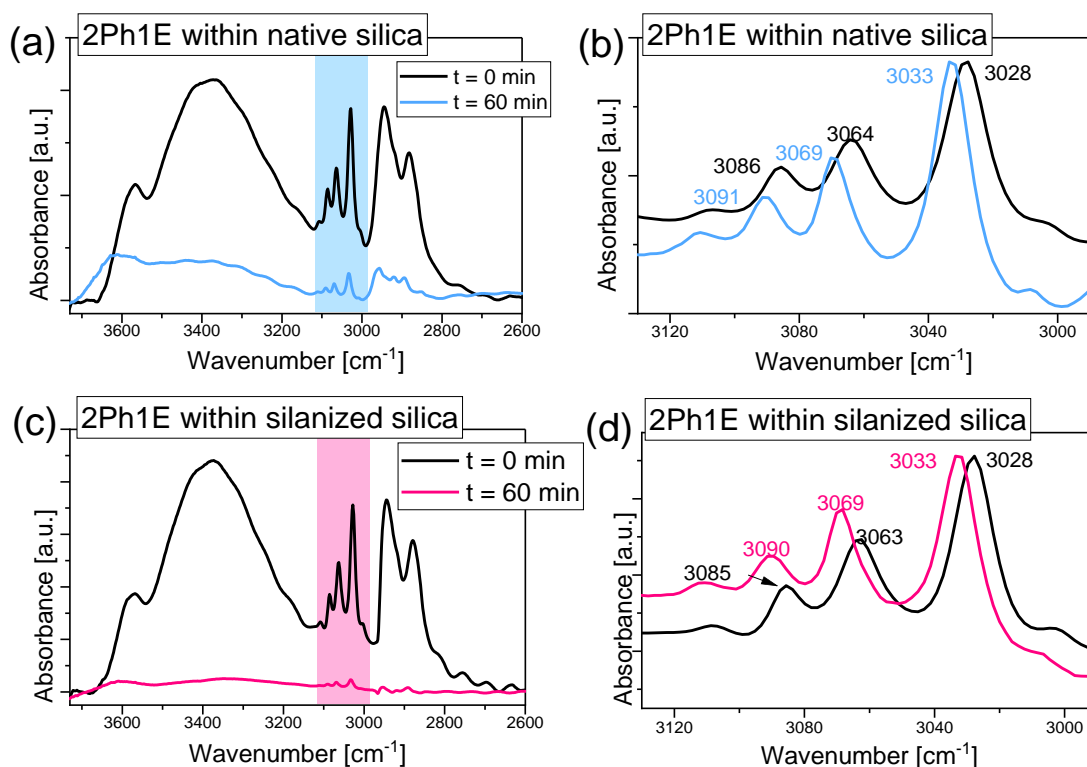


Fig. S7. FTIR spectra of 2Ph1E infiltrated into native (a,b) and silanized (c,d) silica mesopores ($d = 4 \text{ nm}$) at $t = 0 \text{ min}$ and $t = 60 \text{ min}$ in the frequency region (a,c) $3720 - 2600 \text{ cm}^{-1}$ and (b,d) $3130 - 2990 \text{ cm}^{-1}$ ($T = 353 \text{ K}$).

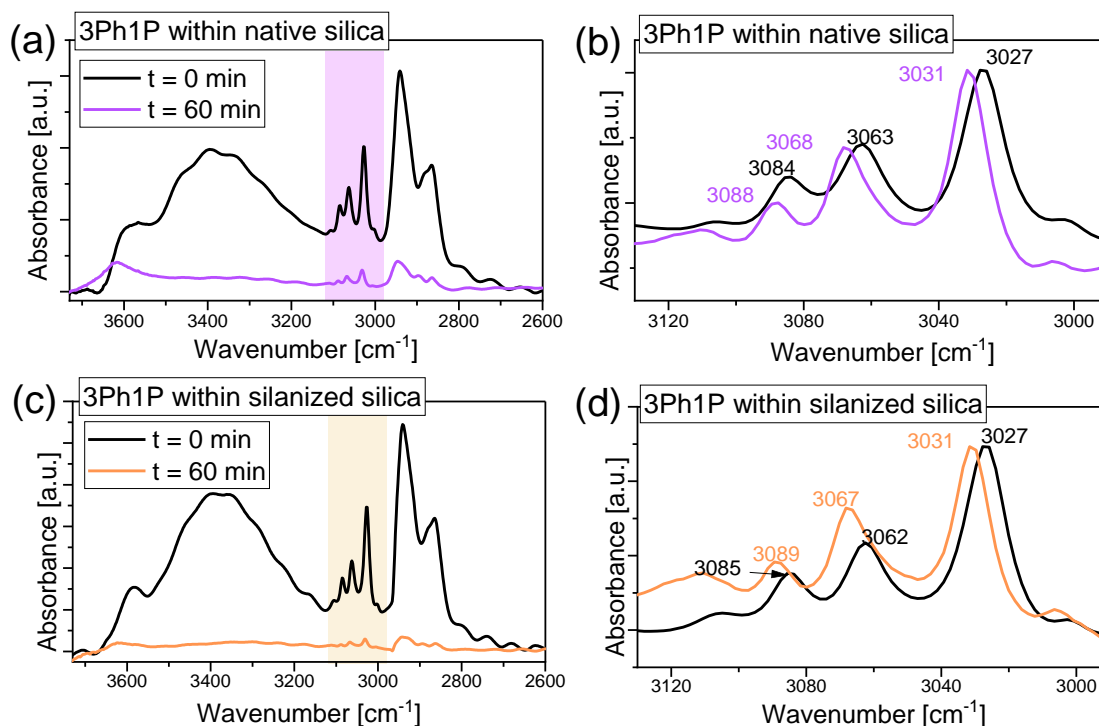


Fig. S8. FTIR spectra of 3Ph1P infiltrated into native (a,b) and silanized (c,d) silica mesopores ($d = 4$ nm) at $t = 0$ min and $t = 60$ min in the frequency region (a,c) $3720 - 2600$ cm⁻¹ and (b,d) $3130 - 2990$ cm⁻¹ ($T = 363$ K).

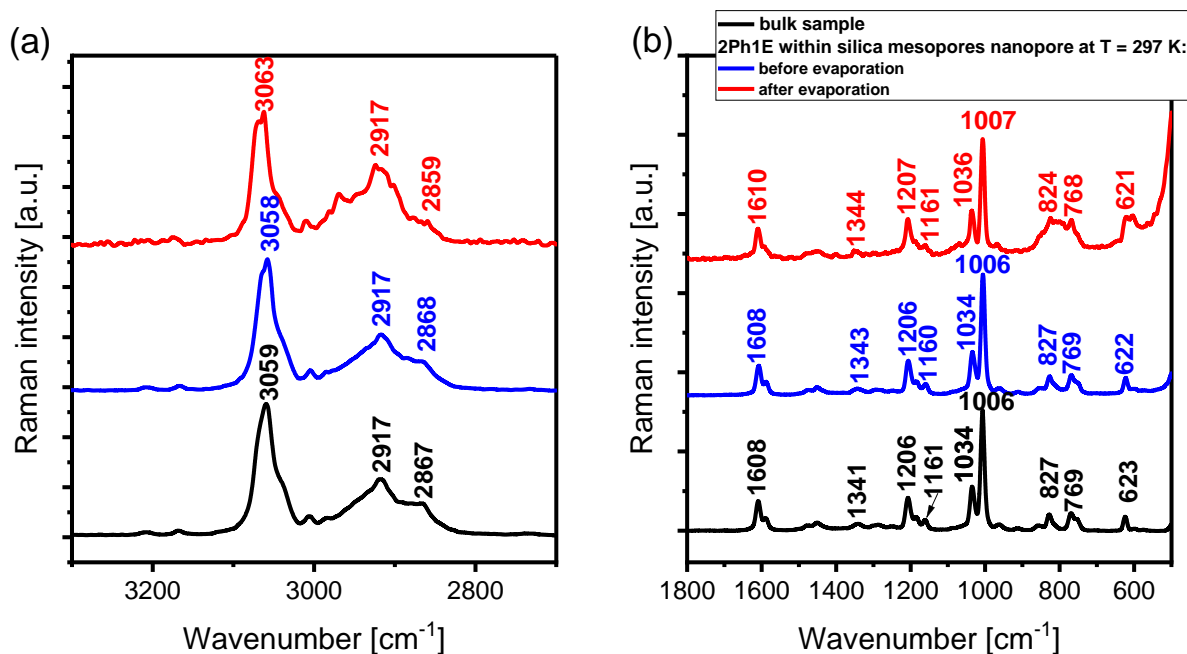


Fig. S9. Raman spectra of bulk 2Ph1E (black), incorporated into silica membrane before annealing (red) and after annealing (blue) presented at 297 K at the frequency regions (a) $3300 - 2700$ cm⁻¹ and (b) $1800 - 500$ cm⁻¹.

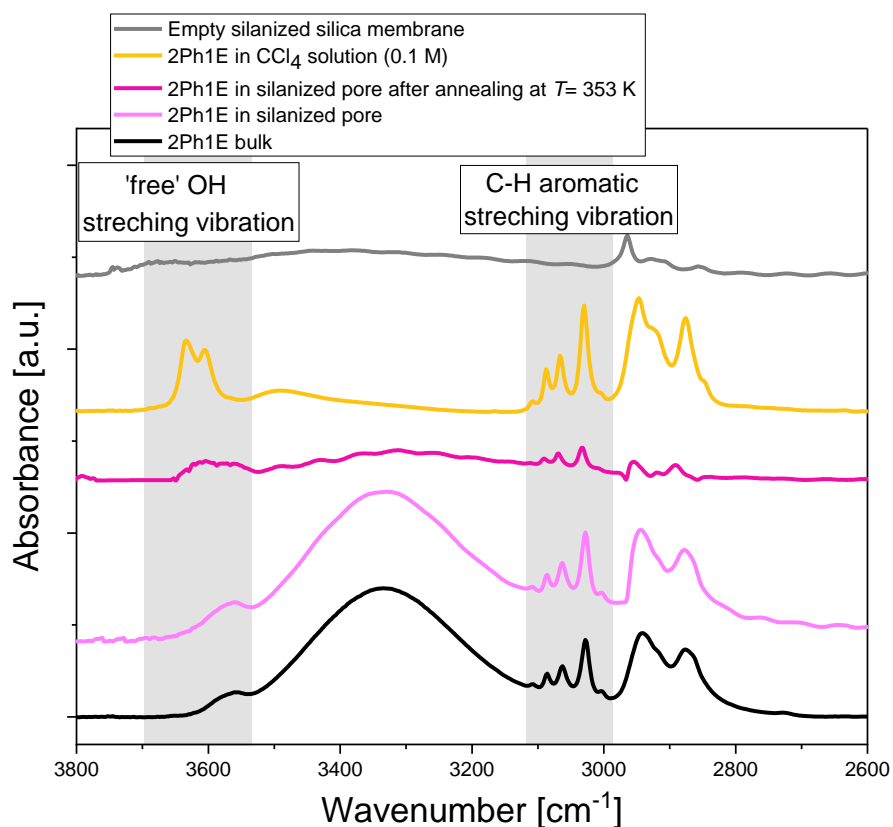


Fig. S10. The comparison of FTIR spectra recorded in the spectral region 3800 – 2600 cm^{-1} at $T = 297$ K of the bulk 2Ph1E, infiltrated into silanized silica mesopores of $d = 4$ nm before and after the evaporation, and 2Ph1E within the 0.1M solution of CCl_4 . For comparison, the FTIR spectrum of “empty” silanized silica membrane was also added. Data for the bulk samples measured within 0.1M solution of CCl_4 were taken from Ref. (1).

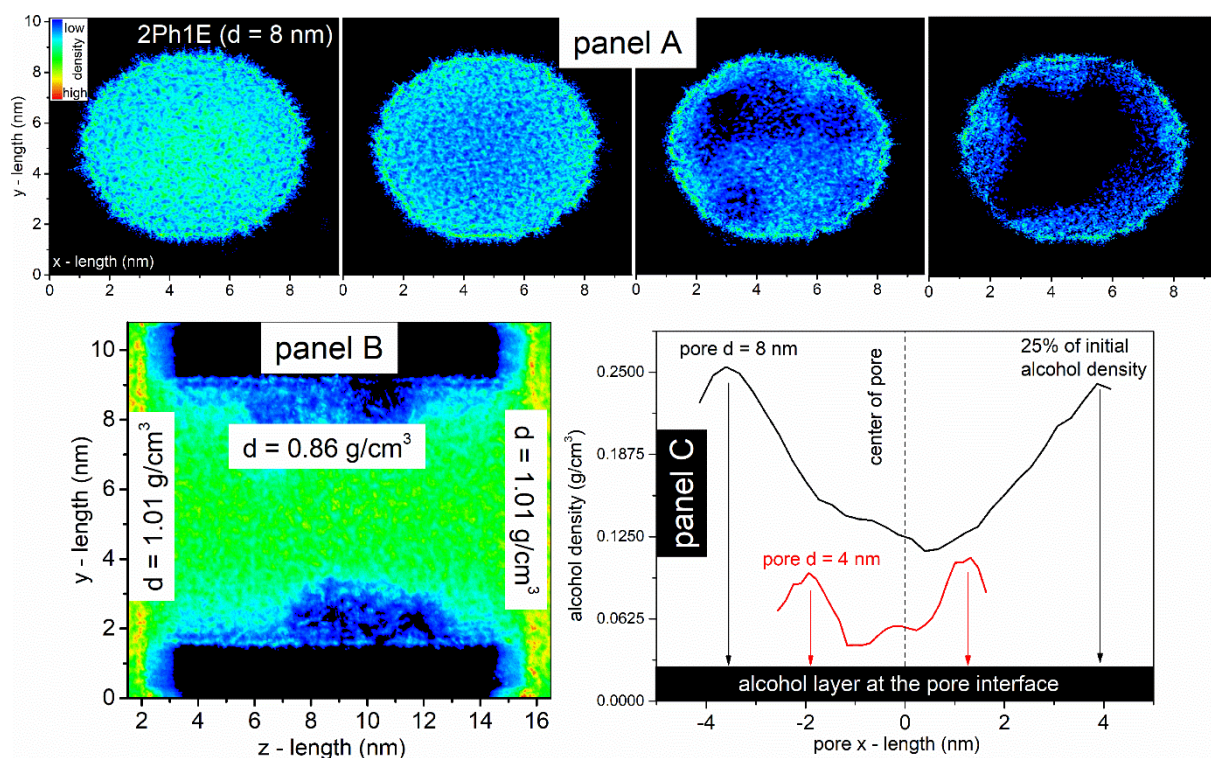


Fig. S11. Panel A: Distribution of 2Ph1E molecules in xy plane of 8 nm pore. From the left side, systems with 100%, 75%, 50%, and 25% of initial pore density have been shown. Panel B: density of 2Ph1E molecules in the pore for the equilibrating NPT system. Panel C: Existence of strongly bonded alcohol layer at the silica interface for both studied pores with 4 and 8 nm diameter, respectively.

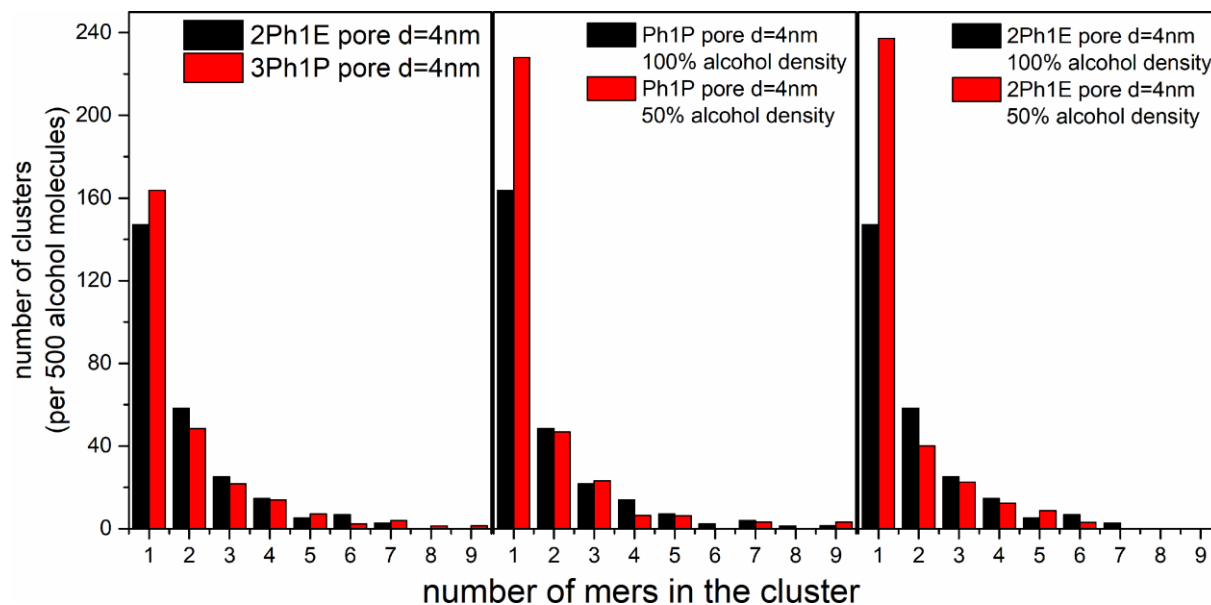


Fig. S12. Histograms comparing formation of clusters in 2Ph1E and 3Ph1P in mesopores with $d = 4$ nm with the 100% and 50% alcohol densities.

Table S1. Average densities of alcohols, and the amounts of free OH groups in the studied systems, i.e. in bulk and pores with diameters of 4 nm and 8 nm.

| Type | Alcohol density (g/cm ³) | Free OH groups (in whole system) (%) | Free OH groups in the pore core region (in alcohol) (%) |
|---------------------------------|--------------------------------------|--------------------------------------|---|
| 2Ph1E bulk | 1.01 | 14.9 | 14.9 |
| 2Ph1E, $d = 4$ nm, 100% density | 0.67 | 6.9 | 29.1 |
| 2Ph1E, $d = 4$ nm, 50% density | 0.33 | 14.3 | 47.5 |
| 2Ph1E, $d = 8$ nm, 100% density | 0.86 | 10.6 | 19.3 |
| 2Ph1E, $d = 8$ nm, 50% density | 0.43 | 18.3 | 27.5 |
| 3Ph1P bulk | 0.98 | 20.6 | 20.6 |
| 3Ph1P, $d = 4$ nm, 100% density | 0.66 | 22.2 | 32.7 |
| 3Ph1P, $d = 4$ nm, 50% density | 0.33 | 30.3 | 45.2 |

References:

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