Supporting Information

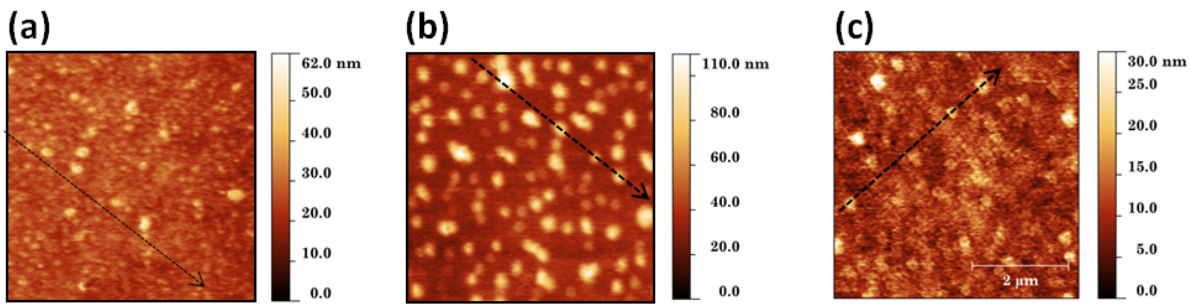


Fig. S1. AFM images of $(HA/PLL)_{24}$ films coated with MG1 (a) and MG2 (b) as measured at 20 ^{o}C. Image (c) shows the surface of the sample (a) measured at 40 ^{o}C.

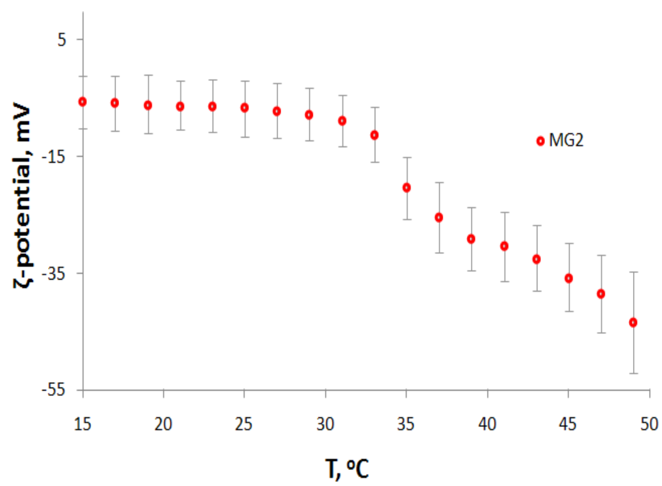


Fig. S2. Zeta-potential of MG2 as a function of temperature.

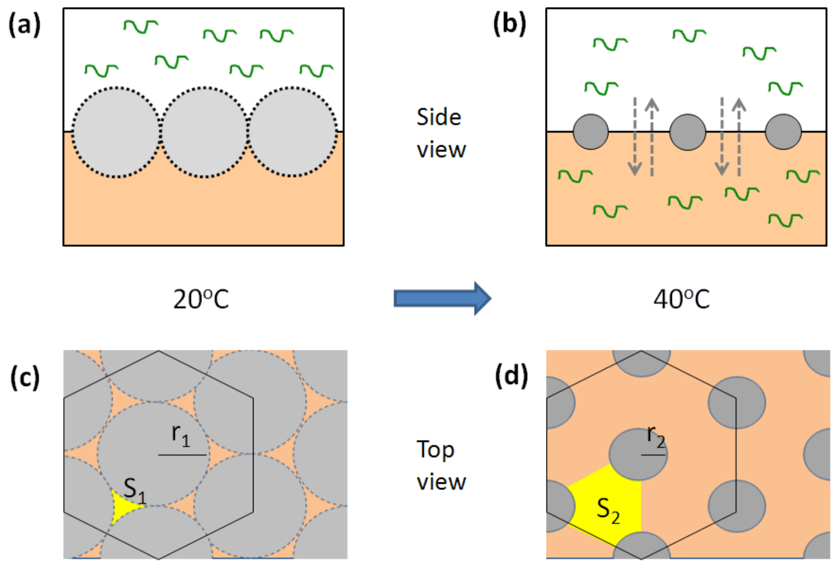


Fig. S3. Schematics (side view) of the PLL diffusion from solution into HA/PLL multilayers coated with pNIPAM microgels at room temperature (a) and 40°C (b). The images (c) and (d) present a top view of the coated multilayers at room temperature and 40°C, respectively. Temperature induced phase transition results in the collapse of the immobilized pNIPAM microgels (reduction of microgel radii from r_1 to r_2) followed by increase of the surface area of the film uncoated with microgels and as a result an enhancement of the PLL diffusion into the multilayers. Hexagonal position of microgels in (c) and (d) shows a single unit of the compactly packed microgels. Surface S_1 and S_2 (highlighted in yellow) represent a free space between the microgels below and above VPTT, respectively.

To the figure S3:

Increase of the available surface between spherical film-adsorbed microgels (S2/S1):

Fig. S3 shows schematics of spherical microgels packed on the mutlilayers (top view) below and above VPTT. Let us calculate the increase of the available surface (S^{20oC}/S^{40oC}). Let us assume that radii of the microgels below and above VPTT are r_1 and r_2, respectively. In the case of compact packing one unit of the packed structure will correspond to a hexagon containing one microgel particle surrounded by six partners (Fig. S3). Rather simple geometrical calculations allow finding a ratio S^{20oC}/S^{40oC} (for details see Supporting Information). In respect to the surfaces S_1 and S_2 (Fig. S1) the S^{20oC} and S^{40oC} can be expressed as the following:

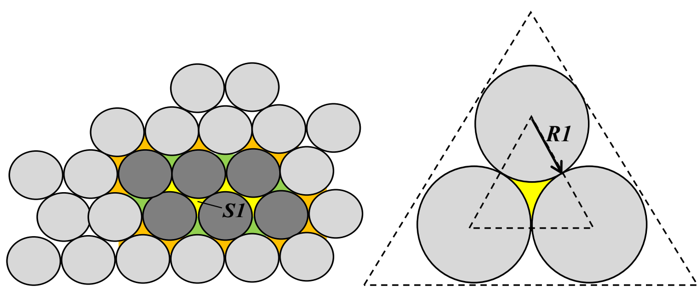
$$S^{20°C} = 2S1$$

$$S^{40°C} = S_{MG}^{20°C} - S_{MG}^{40°C} + 2S1$$

$$\frac{S^{40°\mathrm{C}}}{S^{20°\mathrm{C}}} = \frac{\pi\left(R_1^2 - \frac{1}{4}\cdot R_1^2\right) + (2\sqrt{3}R_1^2 - \pi R_1^2)}{2\sqrt{3}R_1^2 - \pi R_1^2} = \frac{2\sqrt{3} - \frac{\pi}{4}}{2\sqrt{3} - \pi} \approx 8.3$$

Thus, in an ideal packing case the surface available between the microgels when crossing VPTT is enlarged by almost an order of magnitude. This may explain our results demonstrating dramatic enhancement of PLL transport through microgels above VPTT.

More detailed calculations are presented below. In the case of compact packing one unit of the packed structure will correspond to a hexagon containing one microgel particle surrounded by six partners.



For each 6 compact packed particles (see fig. above) as it's assumed for 20˚C surface available for transport is

$$S^{20°\mathrm{C}} = \frac{4(yellow)S1 + 6\cdot\frac{2}{3}(green)S1 + 12\cdot\frac{1}{3}(orange)S1}{6} = 2S1.$$

at 20˚C:

$$S^{20°\mathrm{C}} = 2S1 = 2(S_{triangle} - 3S_{sector}) = 2\sqrt{3}R_1^2 - \pi R_1^2,$$

at 40˚C:

$$S^{40°\mathrm{C}} = S2 = \Delta S_{microgel} + 2S^{20°\mathrm{C}} = S_{MG}^{20°C} - S_{MG}^{40°C} + 2S1 = \pi\left(R_1^2 - R_2^2\right) + 2S1 == \pi\left(R_1^2 - \frac{1}{4}\cdot R_1^2\right) + (2\sqrt{3}R_1^2 - \pi R_1^2).$$

$$\frac{S^{40°\mathrm{C}}}{S^{20°\mathrm{C}}} = \frac{\pi\left(R_1^2 - \frac{1}{4}\cdot R_1^2\right) + (2\sqrt{3}R_1^2 - \pi R_1^2)}{2\sqrt{3}R_1^2 - \pi R_1^2} = \frac{2\sqrt{3} - \frac{\pi}{4}}{2\sqrt{3} - \pi} \approx 8.3.$$