ESI: Nanogels with tailored hydrophobicity 1 and their behavior at air/water interfaces 2 3 Ruiguang Cui^{1,†}, Maret Ickler^{2,†}, Johannes Harrer², Nicolas Vogel^{2,*}, Daniel Klinger^{1,*} 4 [†] co-first authorship 5 ¹ Freie Universität Berlin, Institute of Pharmacy, Königin-Luise-Str. 2-4, 6 14197 Berlin, Germany 7 ² Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Particle Technology 8 91058 Erlangen, Germany 9 * corresponding author: daniel.klinger@fu-berlin.de, nicolas.vogel@fau.de 10 11 **Contents:** 12 Figure S1. Reaction scheme and structure characterization of nanogels. 13 14 Figure S2. Nanogel size distribution calculated from TEM images. 15 Figure S3. Hydrophobicity differences of nanogels as verified by solubility differences of the 16 corresponding polymers. 17 Figure S4. AFM height images of nanogel and cavities after removal of nanogels on PDMA 18 gel matrices. 19 Figure S5. Nearest neighbor distance (NND) distribution of PROPA0 nanogels with 20 increasing surface pressure. 21 Figure S6. AFM phase image of PROPA0 after deposited on a solid substrate from the 22 air/water interface. 23 Figure S7. SEM images of nanogels transferred to silicon water from air/water interface under

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various surface pressure.



Figure S1. (a – b) Reaction scheme to prepare PROPA and DODA nanogels via postfunctionalization of reactive ester precursor nanoparticles. (c) FT-IR spectra verify the complete conversion of reactive esters of the precursor particles to amide bonds of the functionalized particles.

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33 Figure S2. (a-e) Nanogel size distribution calculated from TEM images: PROPA0 to PROPA40,

- 34 respectively; (f) DODA10 and (g) DODA40.
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- 38 Figure S3. Solubility differences of PROPA10 to PROPA40 polymers verify their
- 39 hydrophobicity differences.



41 Figure S4. (a – e) AFM height images of PROPA0 – PROPA40 nanogel on PDMA gel matrices,

42 indicating the protrusion of nanogels in the water phase. (f - j) AFM height images of cavities

43 after removing the PROPA0 – PROPA40 nanogel from the PDMA gel matrices, indicating the

- 44 protrusion of nanogels in the air phase. The scale bars are 300 nm for all images.
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48 **Figure S5.** Nearest neighbor distance (NND) distribution of PROPA0 nanogels with increasing

49 surface pressure, showing a continuous transition towards smaller interparticle distances.



- 51 Figure S6. AFM phase image of PROPA0 which shows a thin corona after deposited on a solid
- 52 substrate from the air/water interface.

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- 55 Figure S7. SEM images of nanogels transferred to silicon water from air/water interface under
- 56 various surface pressure: (a d) PROPA30, (e h) DODA10 and (I I) DODA40.